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ESTIMATION OF PCB CONTAMINATION IN THE TWELVE MILE CREEK ARM OF LAKE HARTWELL USING GIS AND STATISTICAL TECHNIQUES

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ESTIMATION OF PCB CONTAMINATION IN THE TWELVE MILE CREEK ARM OF LAKE HARTWELL USING GIS AND STATISTICAL TECHNIQUES.

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ABSTRACT

The Lake Hartwell and its Twelve Mile Creek watershed were contaminated with polychlorinated biphenyls (PCBs), mainly Aroclor 1016 and 1254, which resulted in a designation as a Superfund site. The Twelve Mile Creek arm is the most heavily contaminated portion of the lake. The Twelve Mile Creek arm of Lake Hartwell was placed on the National Priorities List (NPL) in the year 1990. In the Record of Decision (ROD) by the EPA in 1994, natural attenuation, primarily through burial by uncontaminated sediment, was declared as the chosen remedy to reach the EPA recommended level of 1 µg/g. Several studies have aimed at understanding the concentrations of PCBs in the sediments and the time required for the concentrations to reach the EPA recommended level. This thesis focuses on documenting results of previous and current contamination levels by Geographic Information System (GIS) modeling to predict when the target sediment concentrations will be reached through statistical techniques.

Results from historic (SD points) sampling points were consolidated on a base map in ArcGIS 10.1. From the historic data, it was observed that the average concentration of the entire study area decreased between 1996

and 2013 due to a number of factors with the average concentration in the year 2013 less than 1µg/g. The concentration at SD011 was the highest through the years with its concentrations considerably higher than the EPA recommended level.

Least squares linear regression was performed on the historic data and was integrated on a GIS map to perform spatial interpolation. Inverse distance weighting interpolation (IDW) in ArcGIS was used to estimate PCB concentrations in areas of the lake arm that have not been sampled. The results indicated a decrease in overall PCB concentration with most areas in the lake reaching the EPA recommended level. However, the removal of Woodside-I and -II dams in 2011 increased the PCB concentrations in the lake with the average PCB concentration of the lake increasing after the dam removal.

The top 10 cm of sediment samples from five new points (named BH) and G-30 were collected to perform particle size analysis on each of the sample. Particle size analysis (PSA) was another estimation technique which was used to estimate the concentration of PCBs at the site based on particle size of the top 10 cm at each sampling location. Results of particle size analysis of BH points were incorporated in ArcGIS 10.1 and spatial

interpolation was performed to predict the concentration in the entire arm of the lake. Using PSA, the concentration at G-30 was predicted to be 4.75 µg/g which was more than its concentration of 3.0 µg/g as measured previously in 2004.

Finally, the PCB concentration in the top 10 cm at each BH sampling point was measured by gas chromatography (GC) techniques and compared with the results predicted by the regression and the particle size analysis techniques. A total of 128 congeners distributed over 84 peaks were accounted for in calculating the total PCB concentration at each location. The highest concentration of 3.76 ± 0.12 µg/g was reported at location G-30 which showed an increase in PCB concentration at G-30 compared to 2004. Overall, particle size analysis established a trend of PCB distribution throughout the lake which was validated by the measured concentrations and proved to be a good estimation technique for the prediction of PCB concentration in the collected samples.

DEDICATION

This thesis is proudly dedicated to my parents who have been my strongest source of support and inspiration right from day one of my education. I wouldn’t be where I am today if it was not for their countless sacrifices to provide me with this opportunity to fulfil my dreams.

ACKNOWLEDGEMENTS

First and foremost, I would like to acknowledge the time and effort spent on this project by my advisor Dr. Cindy Lee. Her constant words of encouragement coupled with her dedication to this project are gratefully acknowledged. In Dr. Lee, I found the best advisor I could ever hope for.

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Special thanks to the efforts of Mr. Scott Brame and Anthony Hermann, for their help in sampling sediments during the coldest of winter.

I would like to extend my gratitude to URS Corporation for sharing some of their data regarding the PCB concentration in the Twelve Mile Creek arm of Lake Hartwell.

Special thanks to David Wyker for spending hours working with me in the laboratory. David's expertise in analytical techniques and his willingness to help me out with any problem at any point during the day is immensely appreciated. Thanks to Cynthia Belinga for her help with the extraction

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LIST OF ABBREVIATIONS

Polychlorinated Biphenyls	PCB
Inverse Distance Weighting	IDW
Record of Decision	ROD
South Carolina Department of Health and Environmental Control	SCDHEC
South Carolina District Court	SCDC
Particle Size Analysis	PSA
Bharadwaj- Hermann	BH
Sedimentary Organic Carbon	SOC
Relative Retention Time	RRT
Gas Chromatography	GC
Accelerated Solvent Extractor	ASE
Gas Chromatography-Electron Capture Detector	GC ECD

CHAPTER 1

LITERATURE REVIEW

1.1 INTRODUCTION

Polychlorinated biphenyls (PCBs) are toxic environmental contaminants which have been manufactured for various purposes such as transformers, capacitors and oil based paints beginning in 1929 (Voogt and Brinkman, 1989). PCBs are ubiquitous in the environment due to their Henry's law constant, which allow transport through the atmosphere, and their persistence in sediments, soils and biota. They were commercially manufactured in the U.S. under the trade name of Aroclors (Erickson, 1982) and were widely used in the U.S until 1979, when the EPA officially issued a ban on the manufacture of PCBs due to their adverse effects on the immune system and the nervous system coupled with their low degradation rate (Pakdeesusuk et al., 2003; USEPA, 1994). The deposition of PCBs in the water bodies combined with their low degradation rate has attracted researchers to study PCB contamination and degradation trends at various contaminated sites all over the world.

Despite the cessation of domestic production of PCBs in the 1970s, the problem of PCBs continues to persist in the ecosystem posing problems for

humans directly and indirectly. For example, in the United States, high levels of PCBs were found in the surficial sediments (0-3 cm) of the Hudson River (Feng et al., 1998). A total of 600,000 tons of PCBs were discharged by General Electric in two plants at Hudson Falls and Ft. Edward, New York (Erickson et al., 1982). Similarly, PCB contamination of about 6.8 ppm was found in sediment cores collected from the Depere Dam located on the downstream of Fox River, Wisconsin (Imamoglu et al., 2004). A typical example of PCB contamination outside the United States can be found in the Thane Creek, Mumbai, India. High levels of PCBs were found in the sediments of the Thane Creek, which directly influenced the aquatic population in the creek as reported by Sahu et al. (2008).

1.2 ENVIRONMENTAL FORMS OF PCBS

PCBs were typically manufactured by the chlorination of biphenyl by chlorine gas using iron as the catalyst (Erickson, 1986). Theoretically, 209 congeners of PCBs can be synthesized that differ in the number and location of chlorine atoms around the biphenyl molecule. The basic structure and numbering of PCBs are shown in Figure 1.1. PCBs are either oily liquids or solids and have no smell or taste (USDHHS, 2000). Typically, PCBs cycle between sediment, water and soil; although, PCBs with lower chlorination

(e.g., mono-, di-, and tri-chlorobiphenyls) are more volatile than higher chlorinated congeners and may partition into air. PCBs were manufactured worldwide and were available under several trade names, for example, Aroclor (Monsanto,USA); Clophen (Bayer,Germany); Phenoclor and Pyralene (Prodolec, France) (Erickson, 1997).

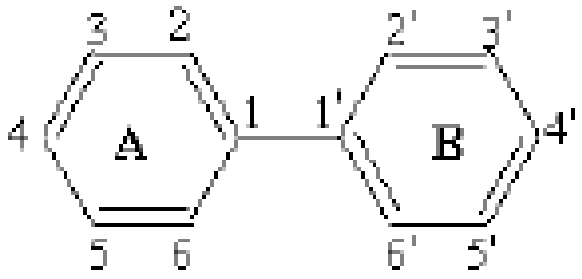
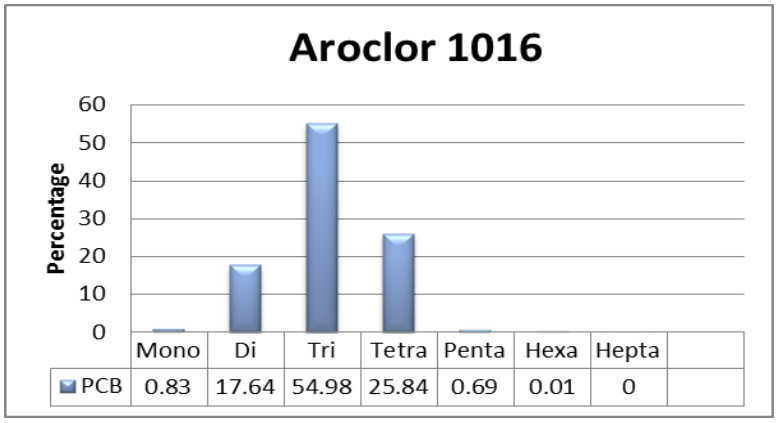
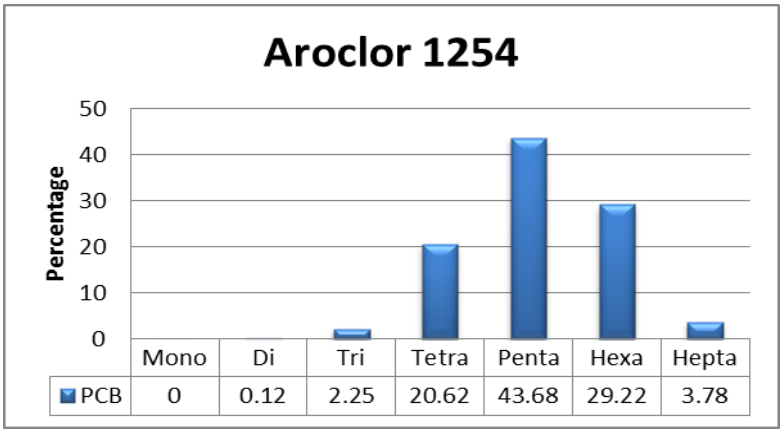


Figure 1.1. The basic structure and numbering scheme for PCBs.
(Adapted from Sivey, 2005)

The Aroclors were a combination of congeners and were marketed commercially based on the weight percentage of chlorine (Erickson, 1982). Figure 1.2 elucidates the configuration of Aroclors – 1254, 1260 and 1016. For these complex mixtures of 1254 and 1260, the chlorination reaction was stopped when the chlorine content reached 54 and 60 %, respectively.

Aroclor 1016 had the least chlorine content (16%) among all the Aroclors and was manufactured by the fractional distillation of Aroclor 1242 (Mayes et al., 1997). The numbers in the x- axis indicate the weight percentage of each homolog in the Aroclor mixture.





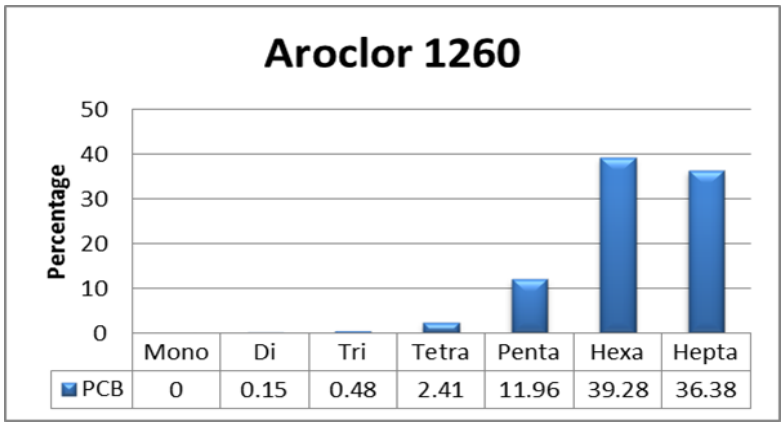


Figure 1.2. Biphenyl homolog distribution in Aroclors – 1016, 1254 and 1260 (Mayes et al., 1997).

1.3 PCBS IN SEDIMENT SYSTEM

When PCBs are discharged into surface water systems, several transport mechanisms may influence their fate (Weber, 2001). PCBs diffuse into air, water or sediment based on congener composition and system temperature (Farley et al., 1994). In general, PCBs are hydrophobic due to high steric hindrance and tend to adhere to sediments (Schwarzenbach et al., 2003). PCB congeners that are more highly chlorinated and have fewer ortho substitutions are less volatile, less water soluble and bind more readily to organic particulate matter.

Sediment consists of particles of different sizes; extensive research has been conducted to study the sorption of sediment organic carbon (SOC) by sediment particles (Karichkoff et al., 1979, Schwarzenbach and Westall, 1981). Barber (1994) observed that sorption of SOC increased with decreasing particle size. He concluded that the SOC was higher in particle size < 63μm which consists of silt and clay due to abundance of magnetic minerals when compared to sediment with particle size >63 μm.

1.4 PCB TOXICOLOGY

The toxicity of PCBs increases with chlorination (Schaeffer et al., 1984). Several PCB congeners have been proved to have highly adverse effects on the nervous system at low concentrations and have also been termed carcinogenic at higher concentrations. Due to their hydrophobic nature and resistance towards metabolism, relatively high levels of PCBs have been reported in fatty tissues of fish (Van den Berg et al., 1998). Literature indicates that PCB uptake in fish can be due to contact with sediment or respiration of water, but the major source is the ingestion of PCB contaminated lower trophic level organisms. Detailed research describing the biomagnification and bioaccumulation of PCBs at each trophic level has been studied elsewhere (Rashleigh et al., 2008; Hansen, 1999; USEPA, 2003).

1.5 ENVIRONMENTAL TRANSFORMATION OF PCBS

The properties of PCBs such as high boiling point, low vapor pressures, hydrophobicity and high bioconcentration factors make them difficult to degrade and increase their its persistence in the environment

(Schwarzenbach et al., 2003). Brenner et al. (2004) identified contaminant weathering as a mode of reducing the impact of PCBs on the environment. Evidence of PCB physiochemical weathering of near surface sediments was found in Lake Hartwell (Farley et al., 1994). Aerobic biodegradation of PCB contaminated sediment has been reported (Abraham et al., 2002) and anaerobic biodegradation of PCB contaminated sediment has also been reported (Pakdeesusuk et al., 2003). Sequential anaerobic-aerobic biodegradation was shown by Amid et al. (1993).

1.6 UTILIZATION OF GIS BASED SPATIAL INTERPOLATION OF CONTAMINANTS

Geographic information systems (GIS) is a powerful modelling tool to develop maps and simulate data to predict past, present and future scenarios. GIS is rapidly paving its way into research work across various fields and has been widely used in the area of environment science and technology (Nadal et al., 2002; Pistocchi, 2008; Pistocchi, 2010). Spatial interpolation is a feature in ArcGIS which helps in predicting unknown values of any geographic point from a limited number of known data. Spatial interpolation is further sub divided into various forms with natural neighborhood, kriging and inverse distance weighting (IDW) being the

commonly used techniques (Bonham-Carter, 1994). The IDW is a moving average interpolator which is based on the assumption that the effect of one point on another diminishes with distance. Natural neighborhood is a technique, which is similar to IDW, but it uses geometric interpolation to allot weights based on proportionate area. It is useful for data points which are unevenly distributed. Kriging is a more advanced technique which utilizes statistical models that incorporate autocorrelation among a group of measured points to create prediction surfaces (Johnston et al., 2001). These techniques of spatial interpolation proved to be very useful in a number of studies which were aimed at modelling contaminant distribution of a site (Jonsson et al., 2003; Perguini et al., 2012; Morio et al., 2010). A typical example of utilizing spatial interpolation in PCB contamination would be in Hudson River (Butcher, 1996) and in ospreys found in Strutgeon Lake, Ontario (de Solla et al., 2008).

1.7 UTILIZATION OF REGRESSION ANALYSIS

Statistical analysis has always been a key step in a wide variety of research. Regression analysis has been used extensively to interpolate and extrapolate unknown values from known data points. It uses a mathematical equation to express a relationship between an independent variable and a dependent variable. Different types of regression analysis are used depending on the data set and the number of independent and dependent variables (Montgomery et al., 2012). Least-squares linear regression (L-R linear regression) is the most commonly used type of regression cited in the literature and is used because it effectively minimizes the sum of square of errors made by every equation (Charnes et al., 1976). Regression analysis to extrapolate contaminant concentration data in the future has been done by several researchers (Stow et al., 1994; Joseffson et al. 2005) Stow et al. (1994) utilized least square regression analysis to estimate aerosol effects on arctic tundra vegetation post-1999, using the data from the year 1990 to 1999. Joseffson et al., (2005) used linear regression to develop a mathematical equation to study the effect of sediment characteristic on the PCB concentrations of the sediment.

1.8 THE TWELVE MILE CREEK ARM OF LAKE HARTWELL SITE

Lake Hartwell and its distributary, Twelve Mile Creek arm, is located in northwestern South Carolina. The former Sangamo-Weston Corporation, a capacitor manufacturing plant, disposed approximately 400,000 lbs of PCBs into the Town Creek from 1955 to 1987. The production and disposal of PCBs into the Town Creek was banned in 1976 (USEPA, 1990). In 1976, the South Carolina Department of Health and Environmental Control (SCDHEC) conducted a broad survey of Lake Hartwell sediments to determine the geographic extent of PCB contamination (Germann, 1988). Later, Germann, in 1987, sampled sediments at different locations in the Lake Hartwell system, and documented the PCB contamination of each location at varying depths. Sediment analysis from this survey suggested that PCB levels were highest in the Twelve Mile Creek arm of Lake Hartwell (Germann, 1988; Sivey, 2005). In 1990, the Sangamo-Weston/Twelve Mile Creek/ Lake Hartwell site was added to the EPA National Priority List. Later, in 1994, the EPA drafted a record of decision (ROD) for this site which indicated monitored natural attenuation (MNA) as the method to be followed to decrease the overall PCB contamination to reach the cleanup goal of 1.0 μg/g (USEPA,

1994). Monitored natural attenuation is a strategy to cover the contaminated sediments downstream with a sufficient amount of clean, uncontaminated sediment such that PCB is prevented from entering the aquatic food chain (Brenner et al., 2004). The natural attenuation process is a combination of reductive dechlorination, burial and volatilization of PCBs, and the EPA hypothesizes that this will decrease the total mass load of PCBs in Lake Hartwell system (USEPA, 1990).

Figure 1.3 indicates the location of sampling sites in the Twelve Mile Creek arm of Lake Hartwell by Germann (Germann, 1988). The site G-30 was sampled again in 1998 (Pakdeesusuk, 2005) and in 2004 (Sivey, 2005) to compare the PCB concentration at G-30 over these years. Figure 1.4 shows the PCB concentration at G-30 calculated by in 1988, 1998 and 2004 respectively. The results indicated that the PCB concentration at G-30 has decreased from 21.1 μg/g in 1988 to 3.0μg/g in 2004. This decrease in PCB concentration can be attributed to monitored natural attenuation.

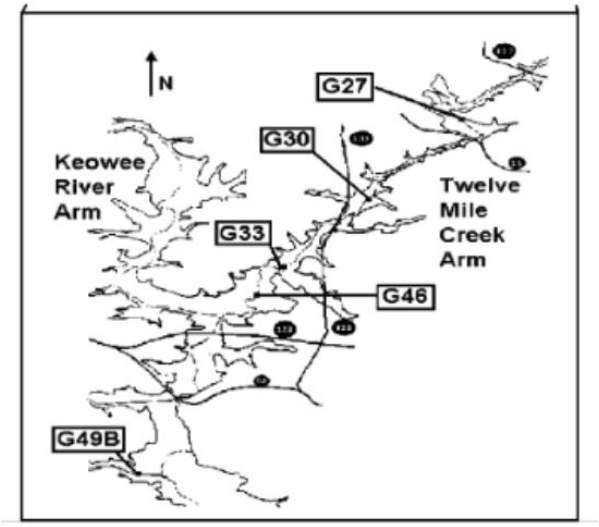


Figure 1.3 Sampling location of Germann in Twelve Mile Creek arm (Germann, 1988)

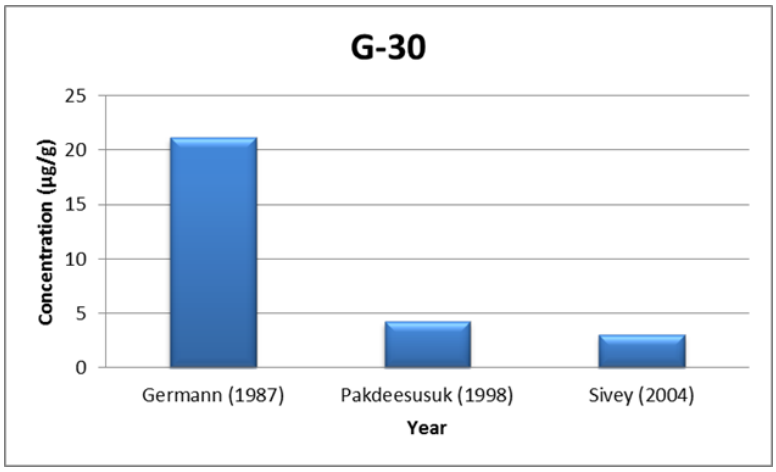


Figure 1.4 PCB concentrations (µg/g) at G-30 in 1987, 1998 and 2004

The SCDHEC sub-contracted the surveying of PCB contamination in the Lake Hartwell system to URS Corporation. The URS Corporation sampled

sediments at various sites across Lake Hartwell. Figure 1.5 displays the sampling sites (known as SD points) in the Twelve Mile Creek arm of Lake Hartwell.

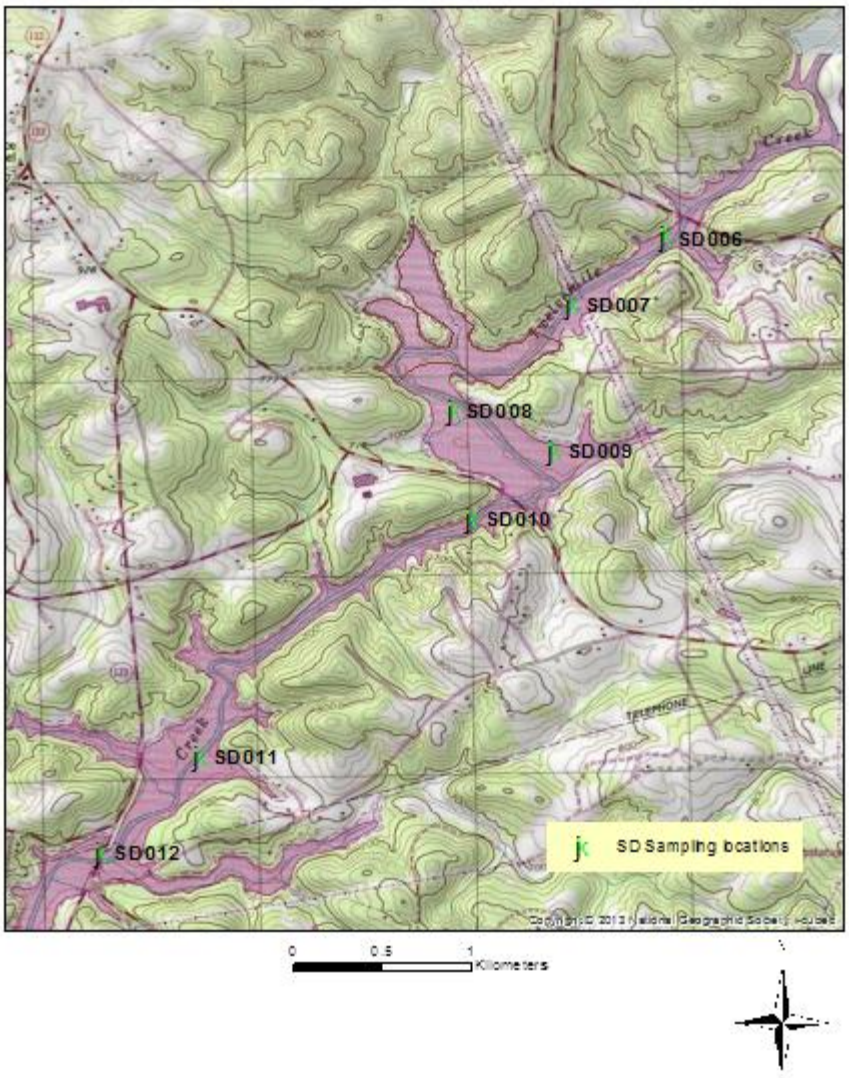


Figure 1.5 Sampling locations by URS Corporations

The Twelve Mile Creek flows southwest to Lake Hartwell. The upper portion of the Twelve Mile Creek contains three impoundments, each associated with a dam (Figure 1.6). The Easley-Central dam is used for public water supply, whereas the Woodside- I and II dams were built in

between 1955 and 1963 for the purpose of hydroelectricity (SCDHEC, 2006). In the year 2011, the United States District Court of South Carolina, Anderson division, passed a verdict which ordered the removal of the Woodside- I and II dams (USDC, 2011) which posed as an impediment to sediment transport.

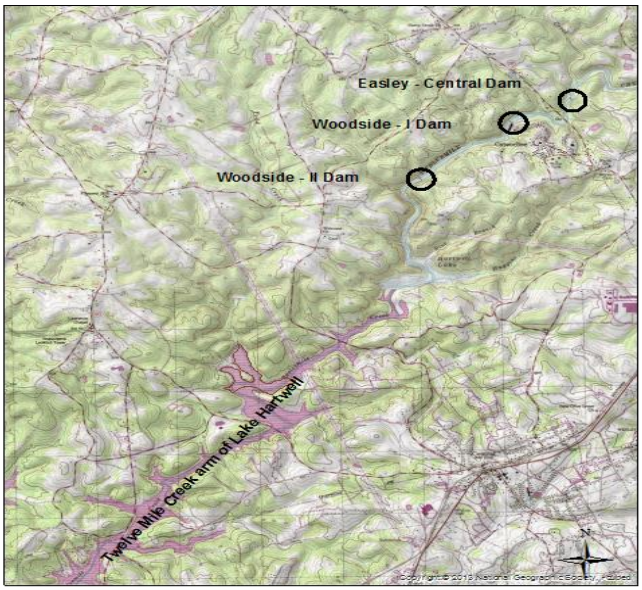


Figure 1.6 Locations of Woodside- I and II and Easley- Central dams.

CHAPTER 2

RESEARCH OBJECTIVES

The primary goal of my thesis was to predict PCB contamination trends in the Twelve Mile Creek arm of Lake Hartwell, SC, using historic data from SCDHEC of the past three decades. The efficacy of the prediction was tested by PCB measurement using analytical techniques. The following objectives were accomplished towards the actualization of the goal:

- Consolidate the PCB concentration data in Twelve Mile Creek arm collected by various researchers at different locations over the past three decades.
- Predict the present day (2014-15) concentration of those same locations using simple regression statistical techniques.
- Collect new samples from Germann (1988) location (G-30) as well as new locations (six in total).
- Analyze the samples to determine the PCB concentrations in the surface sediments.
- Enter the historic and current data into the GIS software and create a map by georeferencing G, BH and the SD points into one final map.

- Apply spatial interpolation techniques to the map to yield a map of PCB concentration in Twelve Mile Creek arm in the present day.

CHAPTER 3

MATERIAL AND METHODS

3.1 CHEMICALS AND SUPPLIES

Acetone was purchased from VWR. Hexane was purchased from Mallinckrodt Chemicals. Isooctane (nanograde) was purchased from Fisher Scientific. Alumina and sodium sulfate were ordered from EM Science. Alumina was deactivated by heating at 500°C for four hours prior to use. Sodium sulfate was dehydrated via overnight heating at 105°C prior to use. Glass wool and disposable glass Pasteur pipettes were purchased from VWR. Standard stock solutions of Aroclor 1016, Aroclor 1254, and aldrin prepared in methanol were purchased from AccuStandard at a concentration of 100 µg/mL in 1 mL vials. Individual PCB congeners, PCBs 14, 169, and 204 prepared in isooctane were also purchased from AccuStandard at a concentration of 100 µg/mL in 1mL vials.

3.2 STUDY AREA

The study area is located in the Twelve Mile Creek arm of Lake Hartwell between Madden Bridge and Interstate-85. There were a total of six

sampling points with one point being G-30 (Germann, 1988) and five new sampling points (BH-1 to BH-5). The study area and sampling points are indicated in Figure 3.1. The BH points were selected randomly with an aim to cover the entire arm of the lake. The figure also includes the location of SD points to indicate the proximity of Bh-1 and SD008, BH-3 and SD009, and G-30 and SD011.

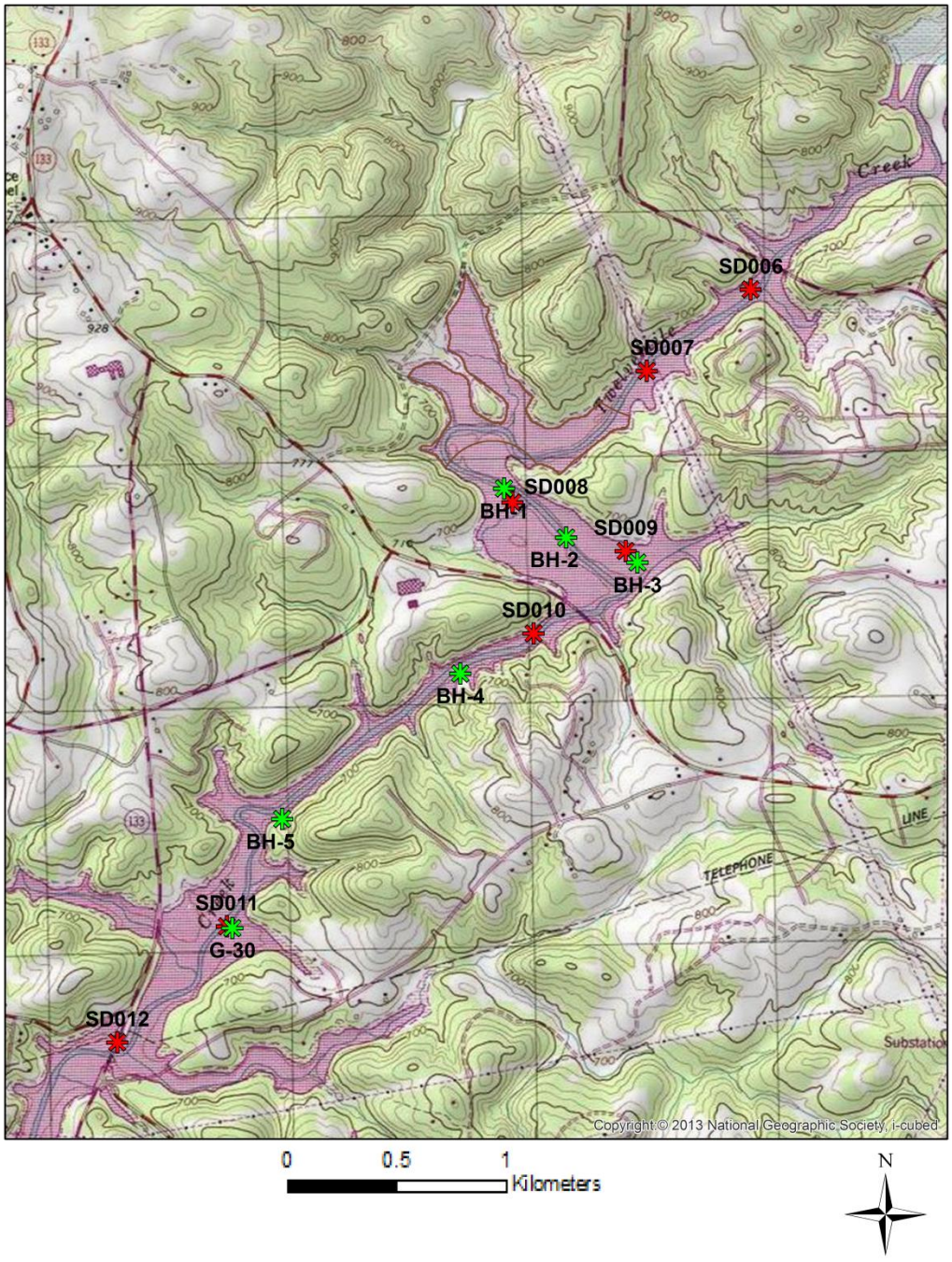


Figure 3.1 Locations for 2015 (BH, green) and for 1995-2013 (SD, red) samples.

3.3 SEDIMENT SAMPLING

Sediment cores were collected using a corer with LexanTM tube (2.5 cm diameter, 76 cm length) fitted at both ends with a PVC cap with extrusions made manually and sections cut with a knife. The LexanTM tube was enclosed in a casing made of stainless steel and the entire setup was attached to a pulley mechanism as shown in Figure 3.2. A dredge sampler (Figure 3.3) was used at sites where the core sampler was unstable. The cores were transported to the L.G. Rich Environmental Research Laboratory (Clemson University, Anderson, SC) and extruded within 24 hours of the sampling event. During extrusion, the cores were sectioned every 5 cm, and stored in clean glass jars (0.5 L) at 4^{o}C prior to analysis. Each 5 cm section was further divided into two equal halves and stored in clean glass jars.

Figure 3.2: Core sampler attached to a pulley

Figure 3.3: Dregde Sampler

Duplicate samples (~5 g each) of all sediment fractions were weighed into aluminum pans and dried at 105^{o}C overnight. The ratio of the dry sediment weight to the wet weight, defined as the dry weight factor, was determined for each sample. Dry weight factors were used to convert wet weights of extracted sediment samples into dry weights so that PCB concentrations could be reported on a sediment dry weight basis.

3.4 PARTICLE SIZE ANALYSIS

Tyler sieves of different mesh sizes (500µm to 4µm) were used to conduct a particle size analysis of the sample. One half of the dried sample from each sampling site was used with a Tyler sieves placed on a sieving machine and were sieved for 10 minutes each. The main motive was to

measure the weight percentage of sand, silt and clay, individually. The sizes used to differentiate the particles were 63µm< sand< 500µm, 4µm< silt< 63µm and clay< 4µm.

3.5 PCB EXTRACTION AND SAMPLE PREPARATION

Extraction of the PCBs from sediment was conducted with an Accelerated Solvent Extractor (Dionex, ASE-200) using 1:1 hexane:acetone solvent (USEPA, 2005). Na_2SO_4 was heated overnight at 105ºC and was added to the other half of the sediment sample to make a total weight of 15 g. The mixture was spiked with 95 µl of recovery standards containing two non-Aroclor congeners (PCBs 14 and 169) at ~2 mg/l prior to extraction. The extracts were blown down to near dryness with nitrogen gas and solvent exchanged in isooctane to make a total volume of approximately 1 ml. The solvent exchanged extracts were stored in GC vials with Teflon-lined septa and crimp tops.

3.6 CONGENER- SPECIFIC PCB ANALYSIS BY GC-ECD

PCB calibration standards were prepared using 1:1 mixtures of Aroclors 1016 and 1254 in isooctane. Total PCB concentrations in the calibration standards were approximately 100, 250, 500, 1000 and 2000 ng/mL. The 2000 ng/mL PCB solution was also used as a check standard during GC analyses. Each calibration standard also contained aldrin (36 ng/mL) and PCB 204 (36 ng/mL) as an internal standard. The recovery standards of PCB 14 and PCB 204 at 2 µg/mL were prepared in isooctane. The recovery standards were chosen according to Sivey (2006).

The sediment extracts were analyzed for PCBs on a HP 6890 gas chromatograph (GC). The column used was a 60 m fused silica capillary column (DB- 5, Restek corporation, Bellefonte, PA; 0.25 mm diameter, 0.25µm film thickness) and a ^{63}Ni electron capture detector (ECD). The GC parameters were slightly modified to the ones used by Dang (2012). An initial oven temperature of 115^{o}C was held for 8 minutes, followed by progressive heating at 15oC/min to 160^{o}C (0.5 min hold time), 2oC/min to 260oC (15 min hold time). Total run time per analysis was 76.5 min. The injector and detector temperatures were set at 250^{o}C and 325^{o}C, respectively. Hydrogen was the carrier gas with a flow rate of 2.0 mL/min. Anode and make up gas flow rates were set at 6.0 mL/min and 60.0 mL/min,

respectively. Split vent flow was 57.5 mL/min. Autosampler injection volumes were 1 µL. Blank GC runs (isooctane) were conducted every five GC samples and the septa was replaced every 30 injections.

3.7 SPATIAL INTERPOLATION USING GIS

Historic data of PCB concentration in the Twelve Mile Creek arm of Lake Hartwell from 1995 to 2013 at seven different sites (SD-006 to SD012) were obtained from URS Corporation. The sampling points were georeferenced into a USA TOPOMAP in the ArcGIS software version 10.1 to determine the co-ordinates of individual sampling points. The co-ordinate system used was UTM_NAD_1983 (2011). The PCB concentrations (µg/g) at every sampling point was entered into a plain text document (.txt) and added onto the ArcMap as a layer file. The PCB concentrations at each sampling point were cataloged by year from 1995 to 2013 and added to the ArcMap individually. The area within the Twelve Mile Creek arm to be spatially interpolated was carefully digitized using polygon structures, unwanted areas were ignored while digitizing. The digitized area was named as Twelve Mile Creek arm polygon and was exported as a layer file and added onto the ArcMap. Once the digitization was done, different spatial

interpolation techniques such as kriging, inverse distance weighting (IDW) and natural neighborhood were performed on the Twelve Mile Creek arm polygon for every year from 1995 to 2013.

3.8 REGRESSION ANALYSIS

Regression analysis was performed for the SD sampling points to predict the PCB concentration for the year 2015. This data set was then used with GIS to perform spatial interpolation and cross referenced with the values determined from the GC-ECD for the year 2015.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 MAPPING OF PCB CONCENTRATION USING ARCGIS

Previously, PCB contamination in the Twelve Mile Creek arm was measured by calculating the PCB concentration of sediment samples from a few locations spread across the lake (Germann, 1988; Farley et al., 1994; Pakdeesusuk et al., 2003; Sivey, 2005; Sivey and Lee, 2007). The number of sampling locations was restricted due to difficulty in accessing certain parts of the lake and the availability of resources. The use of spatial interpolation with ArcGIS provides a method for estimating the PCB concentrations without the time and expense of physical sampling. Of all the spatial interpolation techniques utilized, inverse distance weighting (IDW) proved to be the most stable technique; hence it was used to map the historic PCB data to estimate the concentrations of the entire Twelve Mile Creek arm of Lake Hartwell. The results and the limitations of the estimates are provided below.

The Figure 4.1 shows the average PCB concentration in the entire arm of the lake from the year 1996 to 2013. The average was calculated from the

data collected by URS Corporation on behalf of the SCDHEC from the SD locations shown in Figure 3.1. The figure shows a decreasing trend in PCB concentration over the years and justifies the efficiency of natural attenuation of PCBs. However, there is a small spike in the PCB concentration after 2011, which can be attributed to the removal of Woodside- I and II dams (USDC, 2011) upstream of the lake. The removal of the dams led to the flow of contaminated sediment to Twelve Mile Creek arm leading to an increase in overall PCB concentration in the area

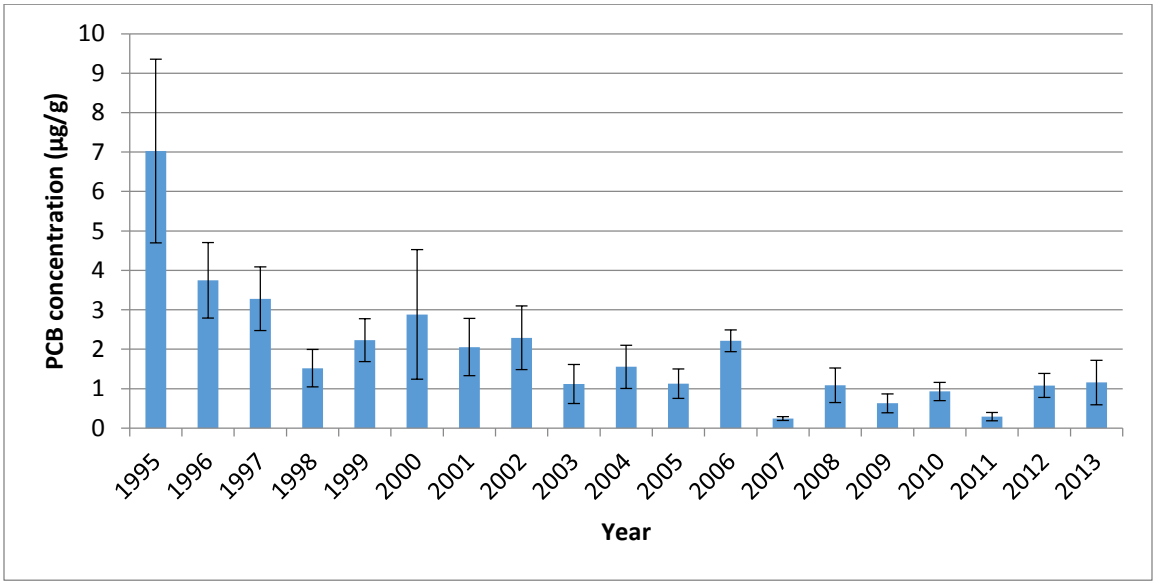


Figure 4.1. Average PCB concentration at Twelve Mile Creek arm from 1996-2013, error bars indicate the range of concentrations in that year

The historic data compiled by URS Corporation was consolidated into a digitized polygon on a GIS map by georeferencing the SD locations from a

base map onto the digitized polygon. Inverse distance weighting (IDW) spatial interpolation technique was performed on the dataset from each year from 1996 to 2013 using the already digitized polygon as the process extent. The map of 1995 was not included because some of the data points for certain locations were missing. Although each year from 1996 to 2013 was evaluated, only select years are included to illustrate the major trends that were observed.

Figure 4.2 shows the PCB concentration distribution in 1996. The highest concentration can be observed at locations SD009, SD011and SD012. For 1996, the highest concentrations were in the range of 5.27 to 7.52 µg/g. The points which are closer to the mouth of the Twelve Mile Creek receive more sediment, which covers and dilutes the contaminated sediment. But less sediment is transported downstream due to the slower velocity of water when the lake widens away from the mouth. The high concentrations at SD011 and SD012 are justified as they are positioned downstream to the other sites. However, a high PCB concentration can be found in SD009, too. Brenner et al., (2004) observed that transect O (which has a similar location to SD009) had the highest sedimentation rate. They also found that mostly silt was deposited in areas surrounding transect O.

Since natural attenuation is dependent on capping of contaminated PCBs with uncontaminated sediment, spots in the lake similar to SD009 may contain higher PCB concentrations compared to other locations in the same gradient.

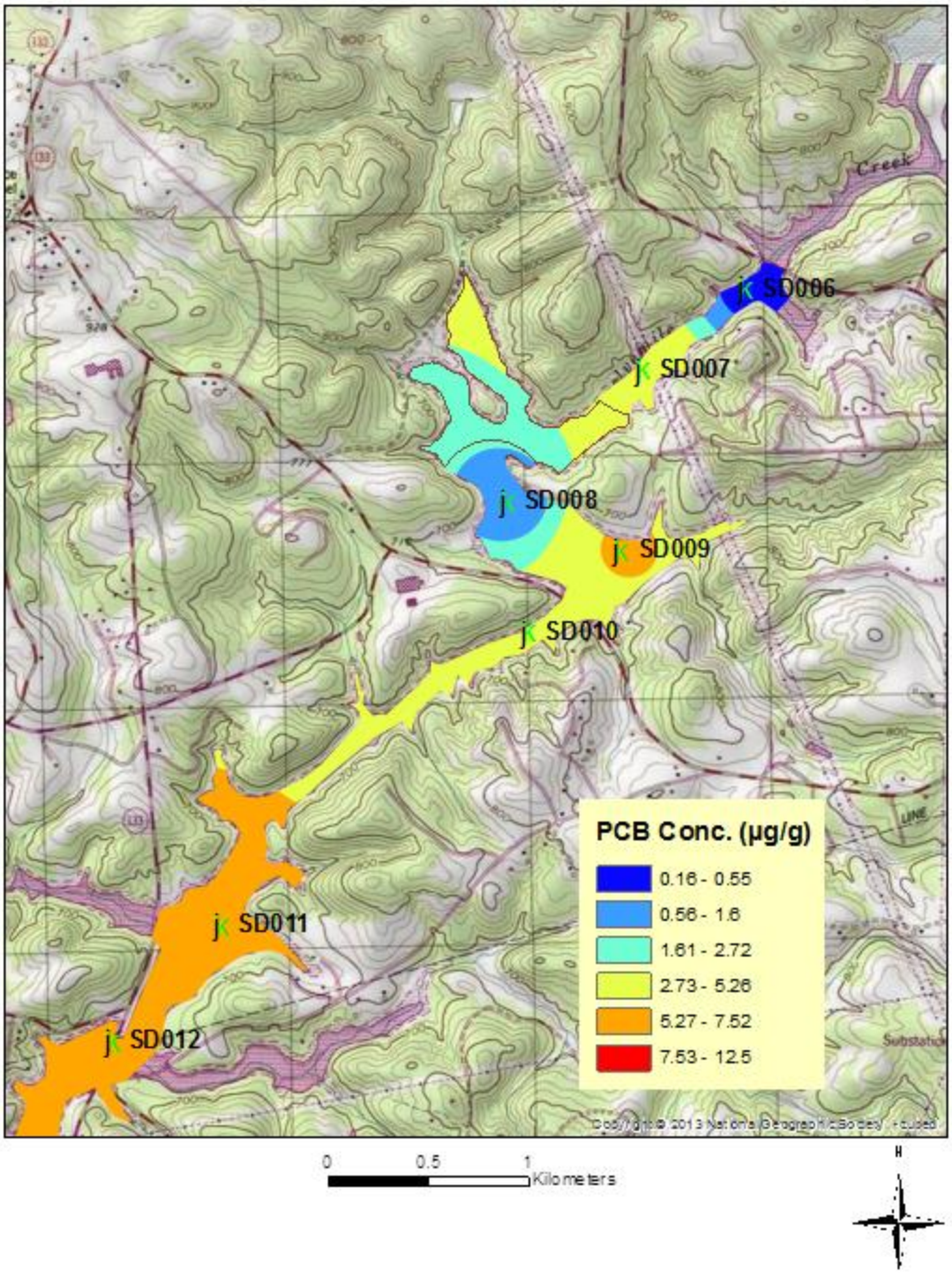


Figure 4.2. Estimated PCB concentration (µg/g) in 1996 using IDW technique

Figure 4.3 represents the PCB concentration distribution in the year 2000. SD011 once again had the highest PCB concentration. In 2000, the estimated highest concentrations shown in red ranged from 7.53 to 12.5 µg/g which was higher than 1996. The average concentration increased when compared to the previous year with SD011 being the main contributor to that increase.

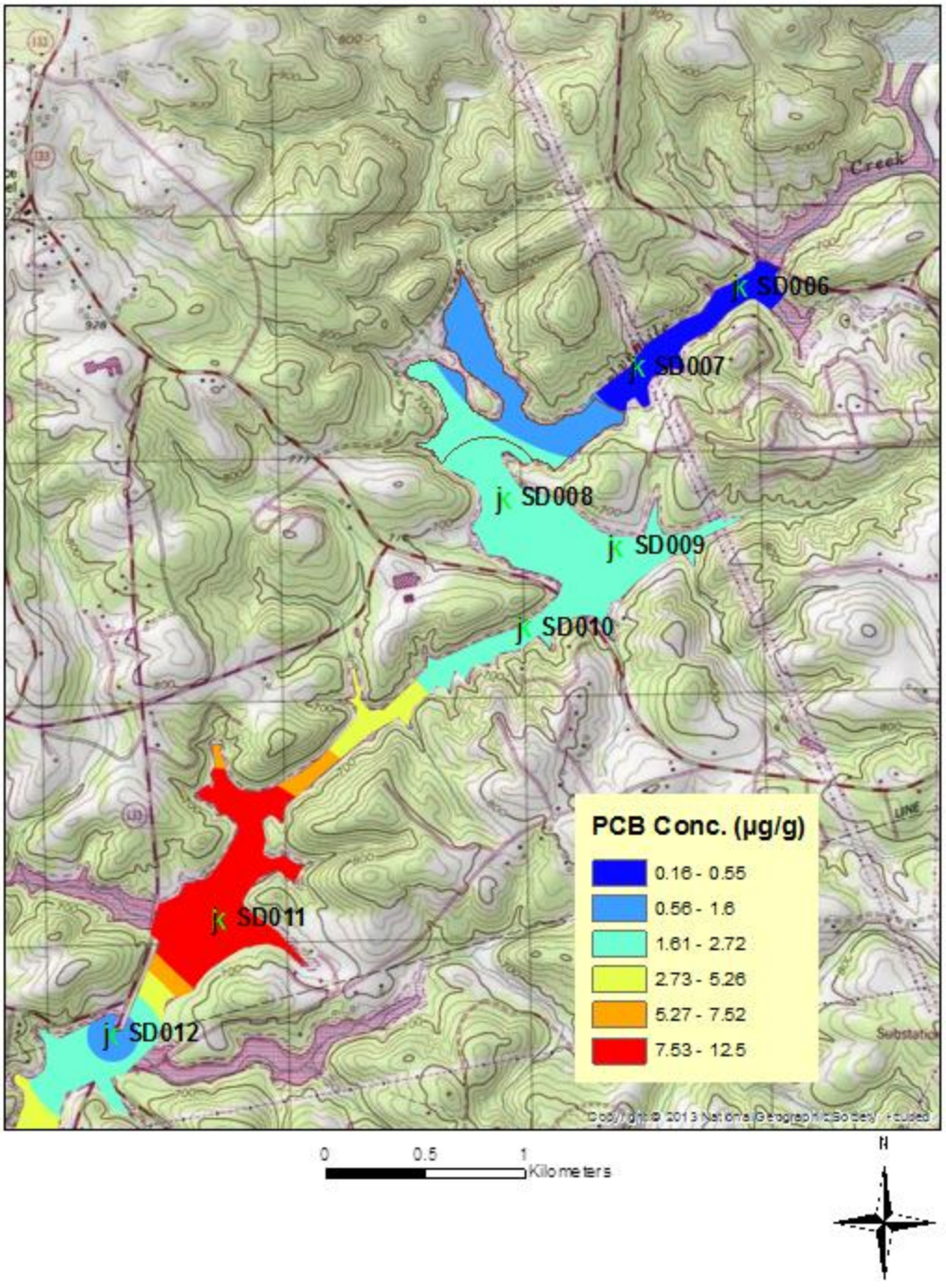


Figure 4.3. PCB concentration in 2000 (µg/g) using IDW technique

Figure 4.4 shows the estimated PCB concentration distribution in the year 2005. The year 2005 followed the trend of overall decreasing PCB concentration. The highest concentrations in 2005 ranged from 1.61 to 2.72 µg/g. SD011 and SD009 continued to have the highest PCB concentrations with SD007 emerging as a hotspot probably due to scouring of sediments at that point.

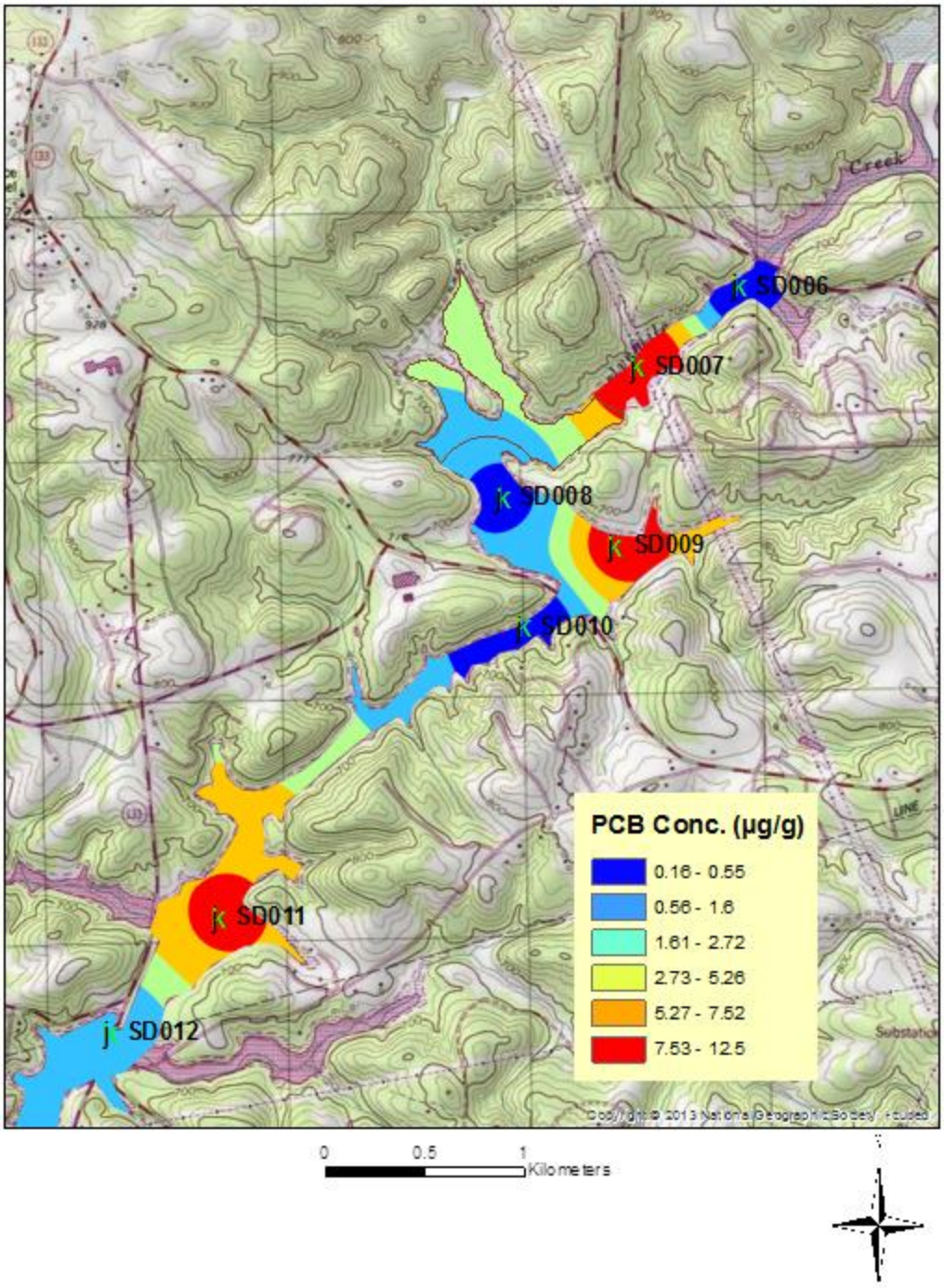


Figure 4.4. Estimated PCB concentration in 2005 (µg/g) using IDW technique

Figure 4.5 displays the estimated PCB concentration in 2010. The year 2010, like its preceding years, displayed a decrease in overall PCB concentration. The highest concentrations were in the range 1.61 to 2.72 µg/g. SD011 continued to have the highest PCB concentration. However, the concentration at SD012 has decreased compared to previous years. Overall, the average PCB concentration in the entire arm of the lake decreased with major portion of the lake approaching clean up level of 1µg/g.

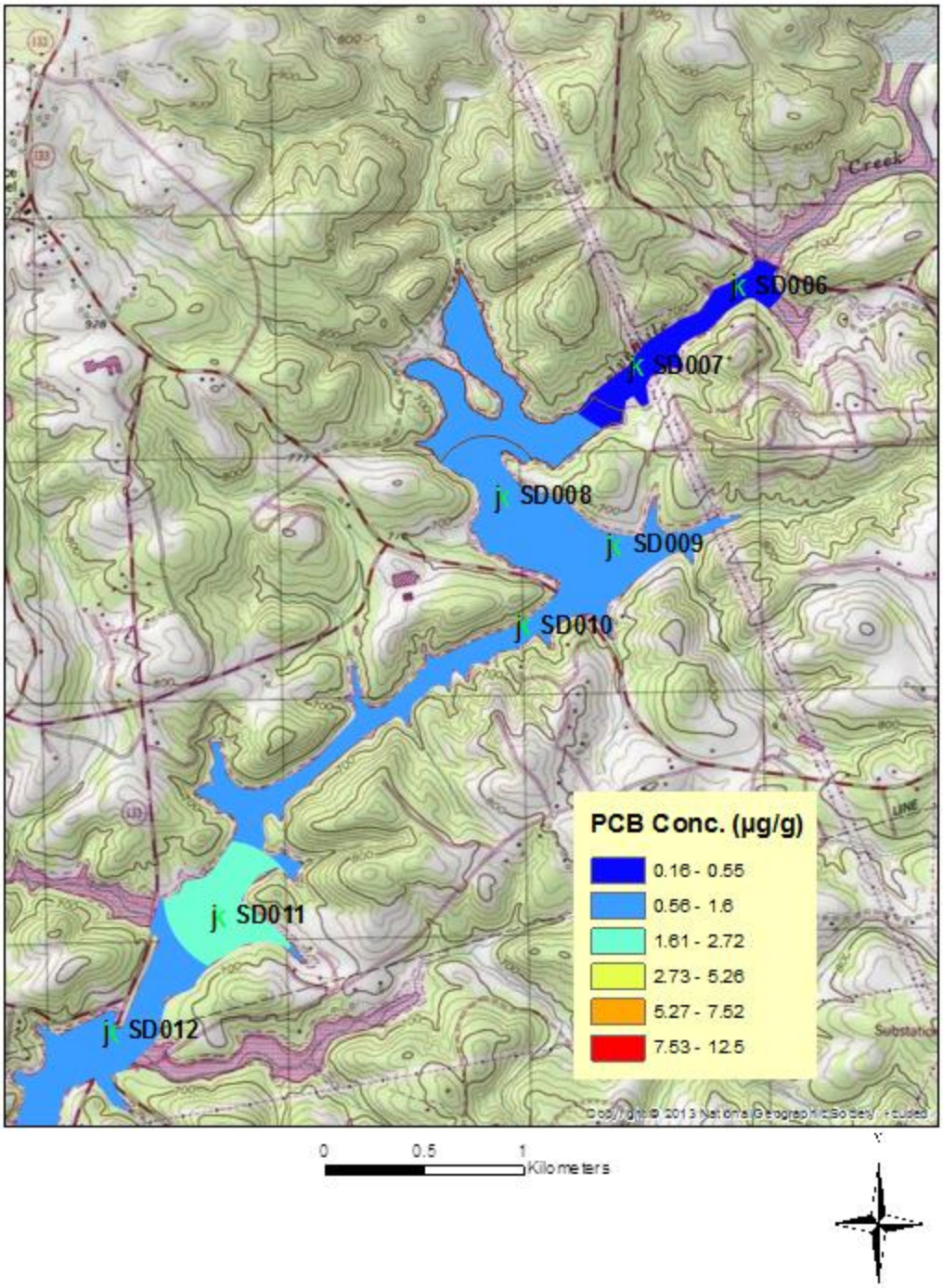


Figure 4.5. Estimated PCB concentration in 2010 (µg/g) using IDW technique

Figure 4.6 shows a change in the estimated PCB concentration trend for 2013. There was a spike in the overall PCB concentrations in the arm of the lake with the highest concentrations ranging from 2.73 – 5.26 µg/g. As usual SD011 had the highest PCB concentration. The spike in the PCB concentration can be attributed to the removal of the Woodside-I and II dams (USDC, 2011). The removal of these dams caused an increase in sediment flux downstream that included contaminated sediment. The lighter silt and clay particles which contain more PCBs per gram have likely moved downgradient and accumulated at SD011. The variation in sedimentation rates (Sivey and Lee, 2007) in different parts of the lake accounts for the change in PCB distribution and concentration.

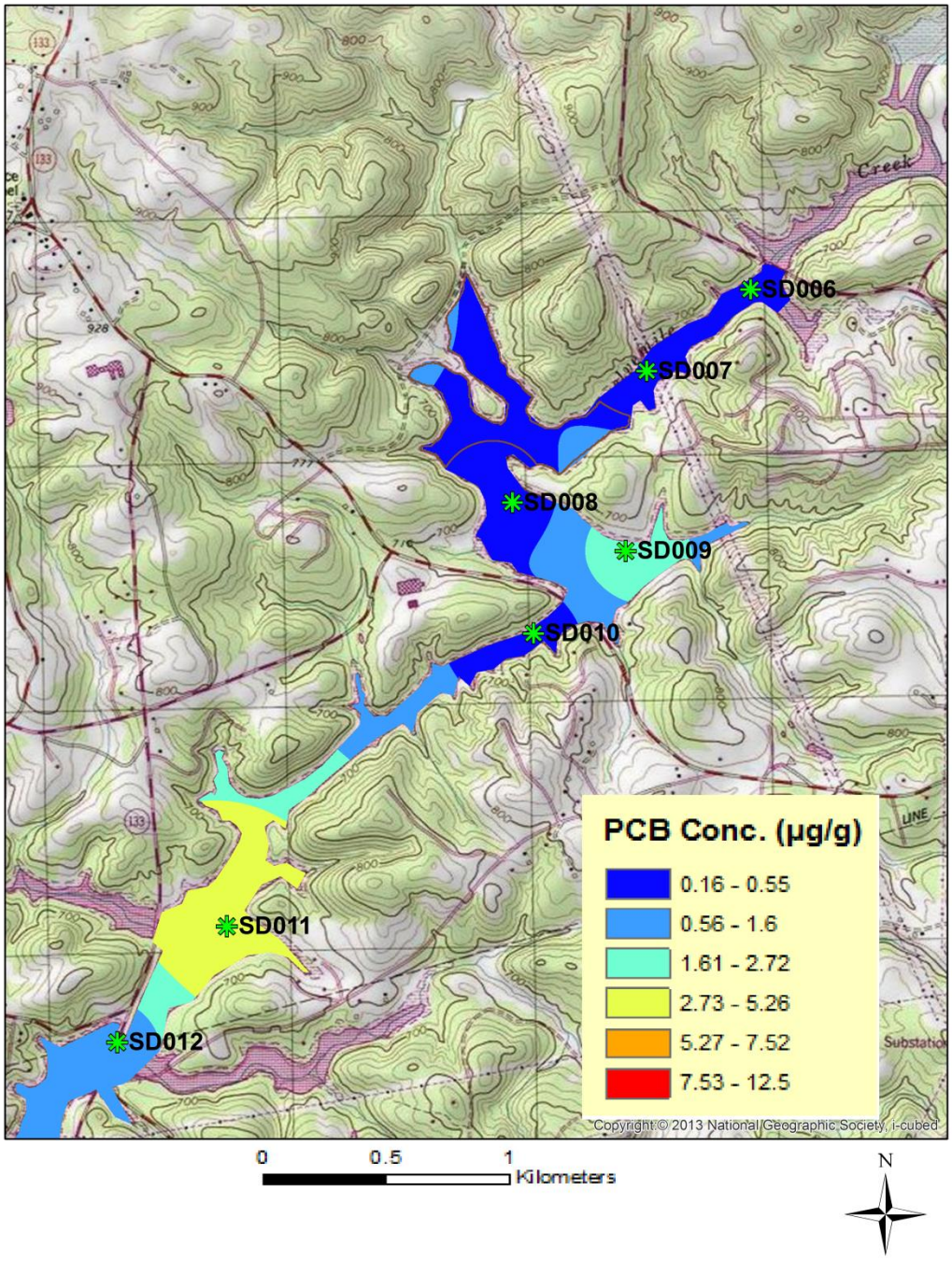


Figure 4.6. Estimated PCB concentration in 2013 (µg/g) using IDW technique

The estimated PCB concentration significantly decreased through the years from 1996 to 2013. The decrease can be attributed to sediment burial, reductive dechlorination, volatilization, dissolution and aerobic biotransformations of PCBs (Farley et al., 1994). The highest PCB contamination area showed a downstream shift over the years. Although, SD011 had the maximum concentration in all years, there was an overall decrease in its concentration. The downgradient movement can be attributed to sediment mixing and cleaner sediment covering up the PCB contaminated sediment upstream. Other factors that may influence the trends in PCB concentrations include variations in annual weather patterns and in sampling. Most of the historic sampling did not use GPS (global positioning satellites) technology, and therefore, locations likely varied from year to year.

However, there was a shift in the trend in 2013. The PCB concentration increased in all the zones when compared to 2010 (Figure 4.5). The increase can be explained by the removal of the Woodside-1 and Woodside-2 dams which led to newer contaminated sediments covering up upstream areas and finer contaminated sediments washed further downstream.

The predicted present day PCB concentration based on regression analysis of the Twelve Mile Creek arm is shown below. Figure 4.7 was prepared by performing least squares regression analyses the historic PCB data.

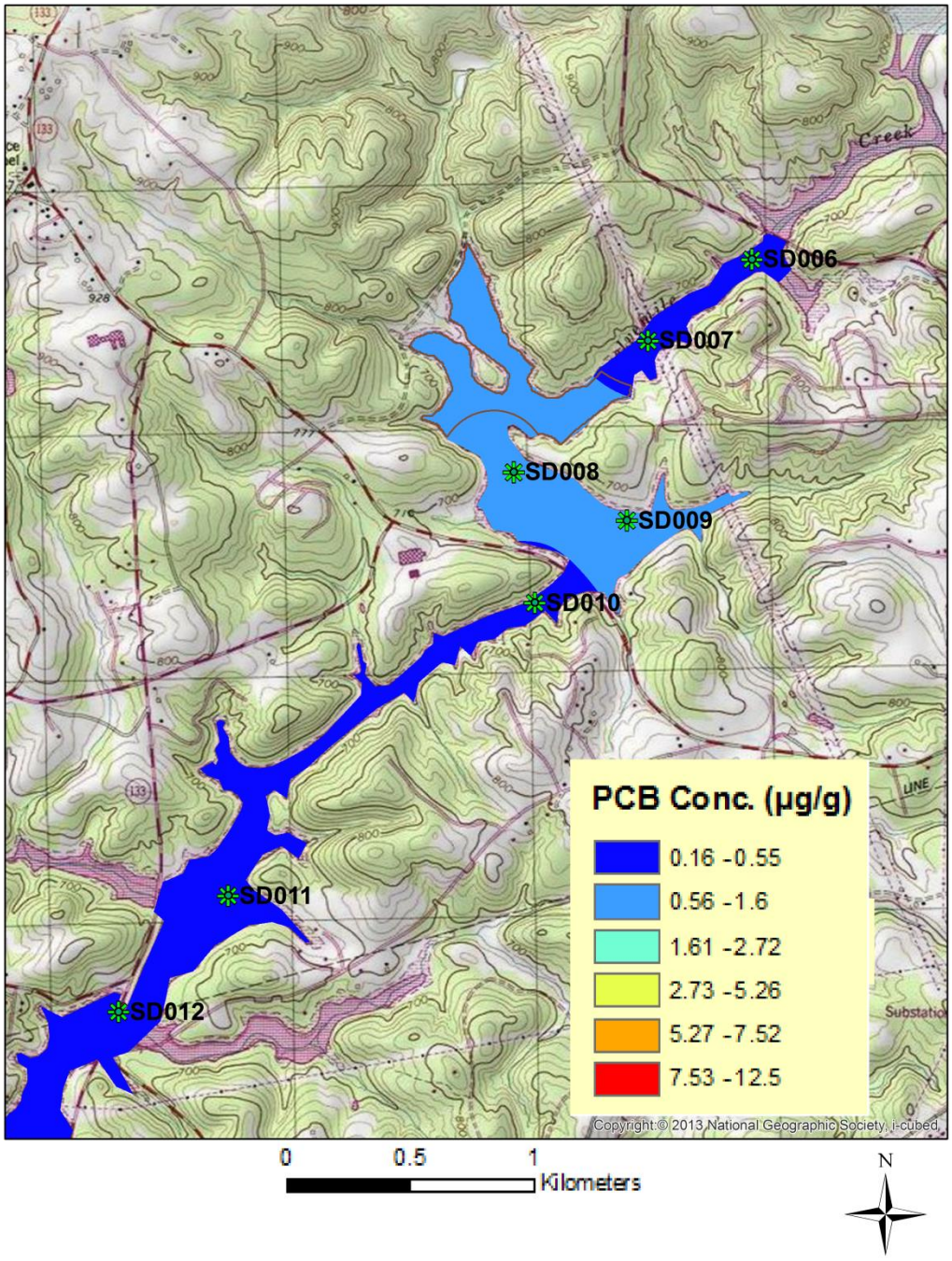


Figure 4.7. PCB concentration in 2015 (µg/g) using IDW and regression technique

The estimated PCB concentration using regression analysis is comparatively lesser than that of 2013. The range for the highest concentrations in the study area was from 0.55 to 1.60 µg/g, suggesting most of the lake was below the EPA recommended level of 1 µg/g. The display area of the map has been extended further downstram to show the increase in PCB concentration towards the main body of Lake Hartwell.

IDW works on the assumption that data points in close proximity to one another are more alike than the ones that are farther apart. The PCB concentration in the surrounding areas of the sampling site would be similar to the site itself due to exposure to similar conditions. One limitation of the IDW is that it does not account for standard error in its calculations. Kriging on the other hand accounts for the statistical correlation between the data points and can provide a more accurate result when compared to IDW. The limitation of kriging is the number of data points. The prediction accuracy increases with increasing the number of data points. Kriging was unsuccessful in this study due to the lack of adequate data points given the size of the lake area studied.

4.2 PARTICLE SIZE ANALYSIS

Particle size analysis was performed for the top 10 cm of all six sediment samples collected in 2015 to calculate their silt and clay composition. Barber (1994) observed that the sedimentary organic carbon (SOC) concentration varied with the size and composition of the sediment particles, with maximum concentration in the silt and clay particles attributed to their surface area and heavy-magnetic mineral content, and an insignificant amount (0.01%) in the sand particles. Barber also observed that a higher concentrations of chlorobenzenes were associated with smaller particle size due to the higher natural organic matter content. Therefore, particle size analysis can be utilized as a rapid estimation technique to correlate the PCB concentration in the sediment sample by estimating its silt and clay content. The site G-30 was sampled in this study due to prior known PCB concentration values of the top 10 cm from Sivey (2005), Pakdeesusuk (2002) and Germann (1988) which are given in Table 4.1.

Table 4.1 G-30 PCB concentration (µg/g) of the top 10 cm in 1987, 1998 and 2004.

Core ID	(1987)*	(1998)**	(2004)***
G30 (µg/g)	21.14	4.22	3.0

*collected and analyzed by Germann in the year 1987.

** collected and analyzed by Pakdeesusuk in the year 1998.

*** collected and analyzed by Sivey in the year 2004.

The top 10 cm of the sediment from G-30 collected by Sivey (2005) was available and analyzed for its sand, silt and clay content. The results are displayed in Figure 4.8

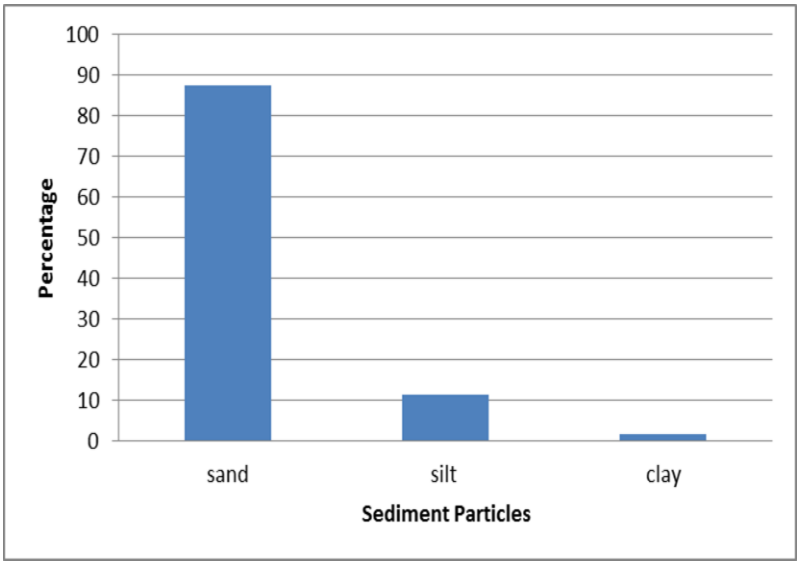


Figure 4.8. Particle size analysis of top 10 cm from G-30, 2004.

The silt and clay content together accounted for 12% of the sediment sample and the measured PCB concentration of that sample was 3µg/g (Sivey, 2005). The concentrations measured by Sivey (2005) can be attributed to the silt and clay fractions based on the results of Barber (1994). Therefore, the silt and clay fractions of the sediment sample from all sites were calculated and compared with that of Sivey (2005) to yield their PCB concentration.

The particle size analysis for the samples from the study area collected in 2015 are listed below. Figure 4.9 shows the particle size analysis of G-30, sampled in 2015. The sediment sample yielded a percentage sand composition of 81%, which is 7% less than the percentage sand composition observed in the same site in the 2004. The decrease in percentage sand composition and the increase in percentage silt and clay composition suggests an increased PCB concentration in the location. This surge in PCB concentration can be explained by the removal of the Woodside- I and II dams in the year 2011 (USDC, 2011). The removal of these dams caused an increase in sediment flux downstream. The lighter silt and clay particles may have moved down gradient, thereby increasing the silt and clay content at the G-30 spot and ultimately, its PCB concentration. The increase in the silt

and clay content in G-30 can be further validated by the estimated PCB concentration map of 2013 shown in Figure 4.6, where the overall PCB concentration increased when compared with the PCB concentration map of 2010 shown in Figure 4.5 with the maximum PCB concentration found at G-30, which is co-located with SD011. The measured value for SD011 also indicated an increase in the G-30 area. Apparently, the location accumulates more silt and clay compared to other sampling locations.

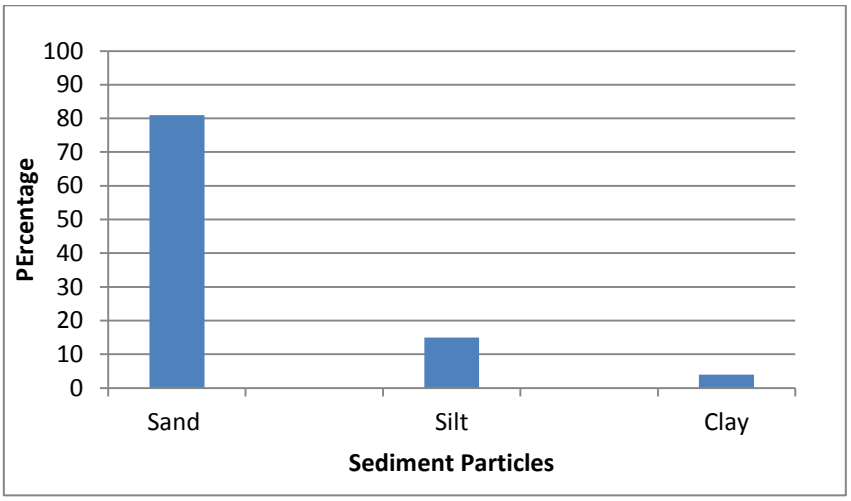


Figure 4.9 Particle size analysis of G-30,2015

Figure 4.10 indicates the particle size analysis for the top 10 cm of BH-1 sediment sample. The percentage sand composition obtained was 94%, which can be explained with the help of Figure 3.1. BH-1 is located up gradient of all the other sampling points. Sand, being the heaviest amongst sand, silt and clay, is transported at the slowest rate downstream when

compared to the other two particle sizes. The apparent difference in the transport of sand, silt and clay accounts for highest sand content at BH-1 and lower sand content in the sites located downstream.

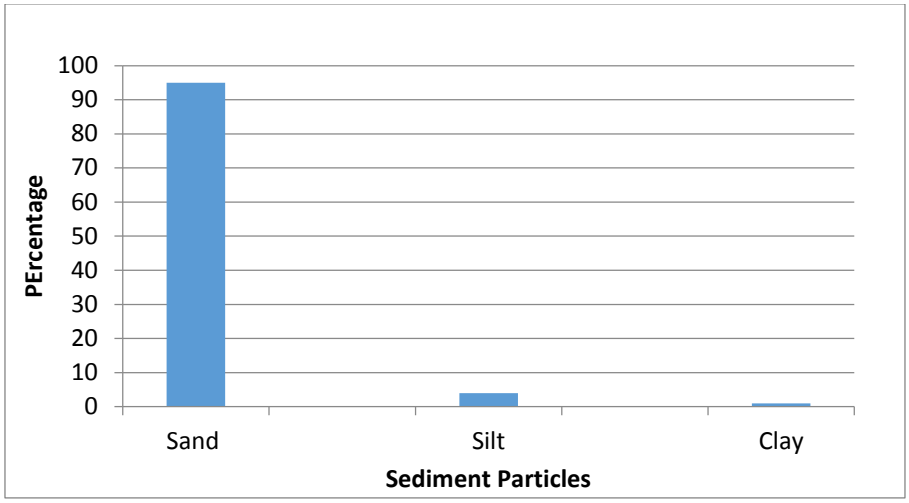


Figure 4.10. Particle size analysis of BH-1

The Figure 4.11 displays the percentage composition of BH-2. The percentage sand, silt and clay composition of BH-2 and BH-1 were almost the same. Typically, a decrease in sand content at BH-2 is expected since its position is further downstream compared to BH-1. The similarity in sediment composition can be attributed to the relatively short distance between the points.

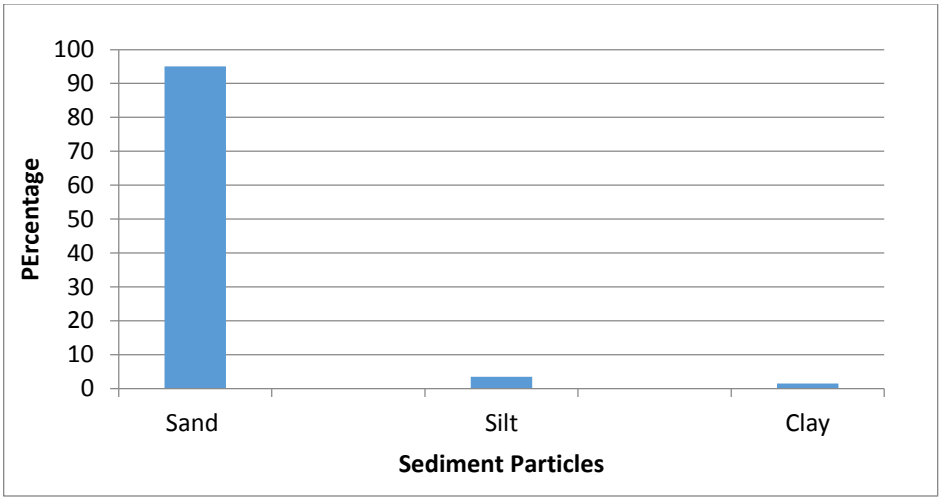


Figure 4.11. Particle size analysis of BH-2

The particle size analysis of BH-3 is shown in Figure 4.12. The sand content was lower than that of BH-2. The lower sand content will result in a higher PCB concentration when compared to BH-2. This result is supported by Figures 4.2 through 4.7 where the PCB concentration of BH-3 (SD009) was consistantly higher than that of BH-2 (SD008).

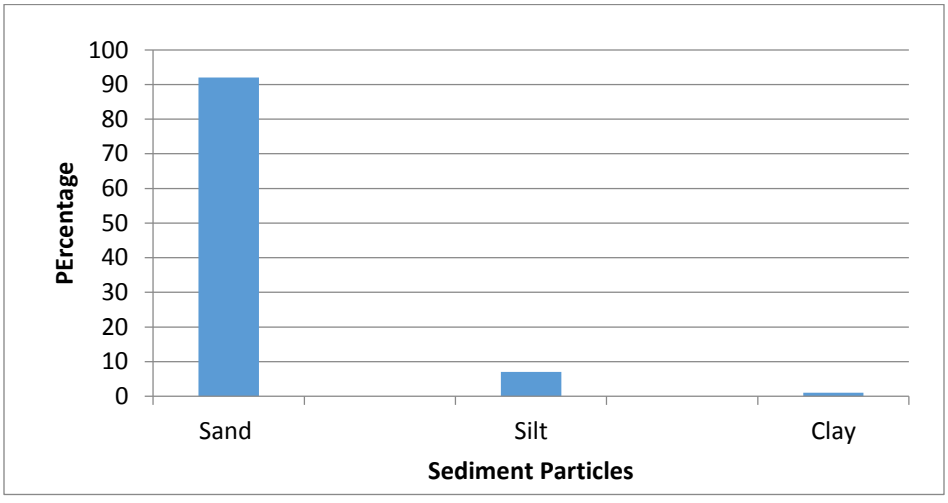


Figure 4.12. Particle size analysis of BH-3

The particle size analysis of BH-4 is shown in Figure 4.13. BH-4 is located further down gradient of BH-3. Typically, the sand content in BH-4 should have been lower than that of BH-3. The distance between the two sites is long enough to account for a considerable decrease in sand content, but the particle size analysis revealed the exact opposite. One possible explanation could be the fact that although BH-4 lies down gradient of BH-3 and should have a lesser sand content, BH-4 lies in the center of the water flow where the velocity is maximum. The higher velocity at BH-4 would discourage deposition of sand. Figures 4.2 through 4.7 add clarity to this explanation; the IDW analysis indicated that the estimated PCB concentration was higher at BH-3 (which is located in the same area as SD009) than its surrounding areas.

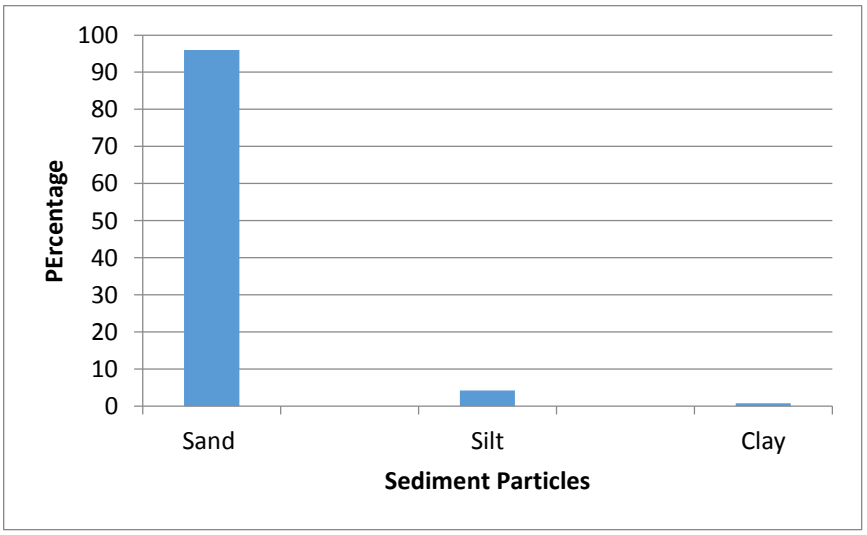


Figure 4.13. Particle size analysis of BH-4

Figure 4.14 indicates the particle size analysis of site BH-5. The results showed a marked decrease in the percentage sand composition compared to BH-4. This is justified because it is positioned downstream of BH-4 thereby providing less access to the sand from upstream.

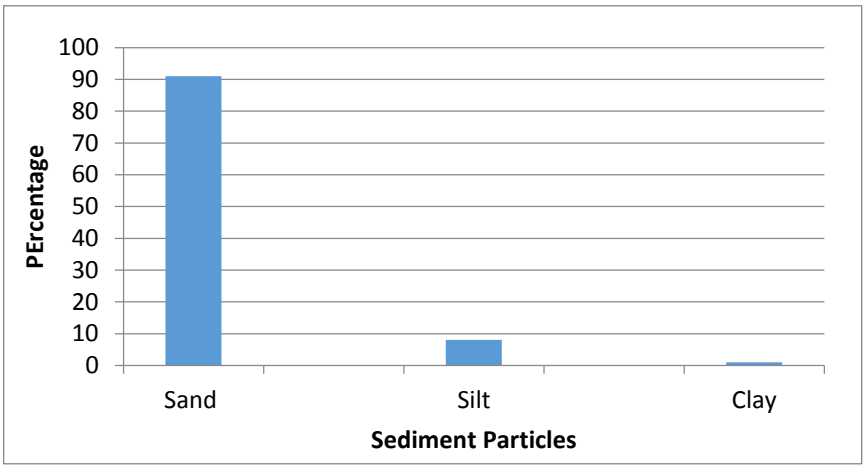


Figure 4.14. Particle size analysis of BH-5

Based on the silt and clay content of the sediment sample from each site, PCB concentrations were predicted by calculating the PCB concentration of 1g of silt plus clay in the sample collected at G-30 in 2004 and multiplying it with the total grams of silt plus clay in the other six locations. The predicted values are given below in Table 4.2.

Table 4.2. Predicted PCB concentration values of sediment samples

Site	PCB concentration (µg/g)
BH-1	1.25
BH-2	1.50
BH-3	1.73
BH-4	1.00
BH-5	2.25
G-30	4.75

The least silt and clay content was observed at site BH-4, therefore it was predicted to have the least PCB concentration among all the samples sites. The highest silt and clay content was observed at site G-30 (SD011).

Triplicate analysis was performed for each sample to determine the error due to loss of sediment mass after each analysis. The error was found to be less than 0.2%. Efficiency can be increased by using parafilm on the outer walls of the sieves which will reduce the loss of smaller particles when the sieves are separated

4.3 PCB QUANTIFICATION

PCB quantification was done to verify the concentrations predicted by the particle size analysis and regression techniques for 2015. The PCBs from the top 10 cm of sediment samples from all six sites were extracted using an ASE-2000 and analyzed using a GC-ECD. The calibration standard procedure and the peak identification are included in Appendix- A and B, respectively.

4.3.1. PCB concentration at BH-1

The top 10 cm of the sediment sample from BH-1 was analyzed and its PCB concentration is shown in Figure 4.15. The PCB concentration in 0-5 cm was marginally less than that in 5-10 cm. The average PCB concentration for the sample was 0.69 µg/g. This low value is justified by the location of BH-1 since it is located further upstream, than other samples, and deposition of less contaminated sand from upstream has lowered its total PCB concentration.

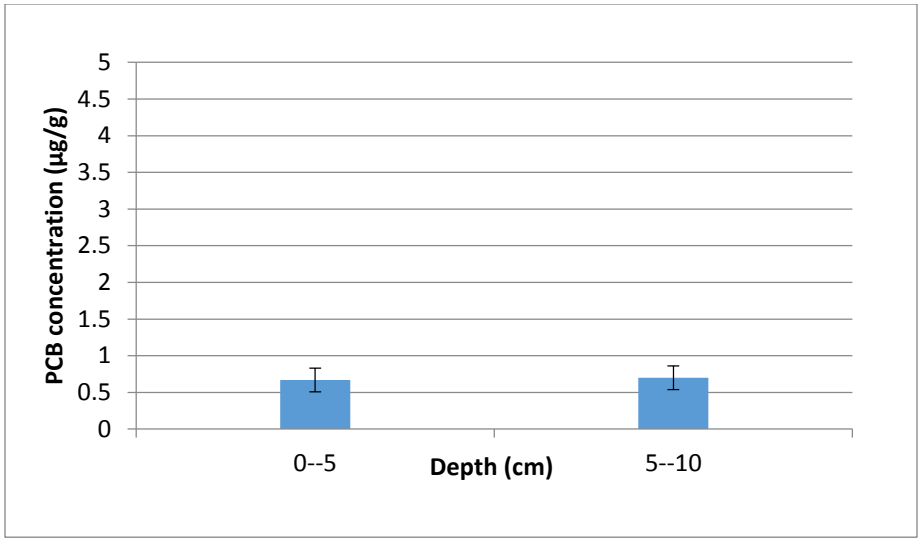


Figure 4.15. Section wise PCB concentration at BH-1. Error bars display the standard error (n=2)

4.3.2. PCB concentration at BH-2

Figure 4.16 displays the measured PCB concentration at BH-2. Similar to BH-1, the PCB concentration in the top 5 cm was marginally less than the next 5 cm, although this difference was greater than the difference between individual sections at BH-1. The average concentration of the two sections amounted to 0.76 µg/g. Although the difference in PCB concentrations between BH-2 and BH-1 is minimal, the slight increase in PCB concentration was due to the downgradient positioning of BH-2 when compared to BH-1. As discussed previously, the downgradient position of BH-2 decreased the sand deposition, hence increased the PCB concentration.

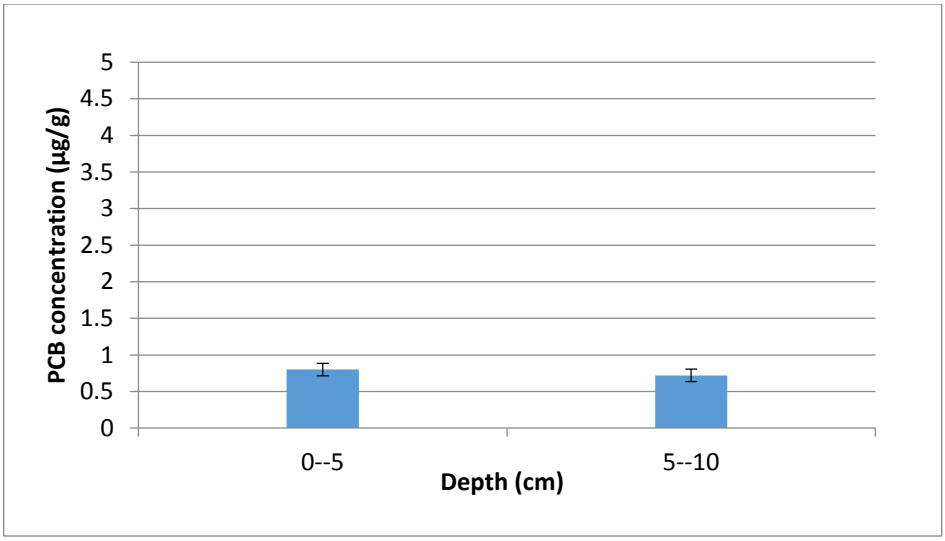


Figure 4.16. Section wise PCB concentration at BH-2. Error bars display the standard error (n=2)

4.3.3. PCB concentration at BH-3

The average PCB concentration of both sections at BH-3 is 1.69 µg/g. Figure 4.17 includes the PCB concentration distribution by 5 cm. Interestingly, the PCB concentration of the top 5 cm is marginally higher than the next 5 cm. A possible explanation for this deviation from the trend observed in the first two samples could be the relatively lower flow rate of sediment particles at BH-3 when compared to the other sampling sites, which has already been discussed in section 4.2. Another reason could be due to analytical error while performing congener specific analysis.

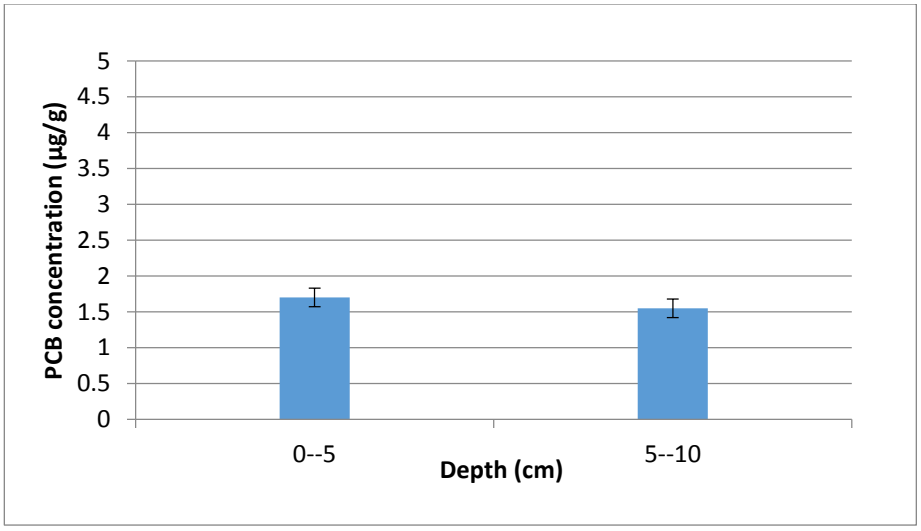


Figure 4.17. Section wise PCB concentration at BH-3. Error bars display the standard error (n=2)

4.3.4. PCB concentration at BH-4

BH-4 is located further downstream in the arm of the lake. The PCB concentration for sites BH-1 through BH-3 followed an increasing trend downstream. However, this was not the case at BH-4. Although, the PCB concentration at BH-4 was greater than that of BH-1 and 2, it was considerably lesser than BH-3. This is due to lower fractions of silt and clay compared to BH-3. Figure 4.18 shows the section wise PCB concentration at BH-4. The average PCB calculated by the congener specific analysis of both section amounted to 1.13 µg/g.

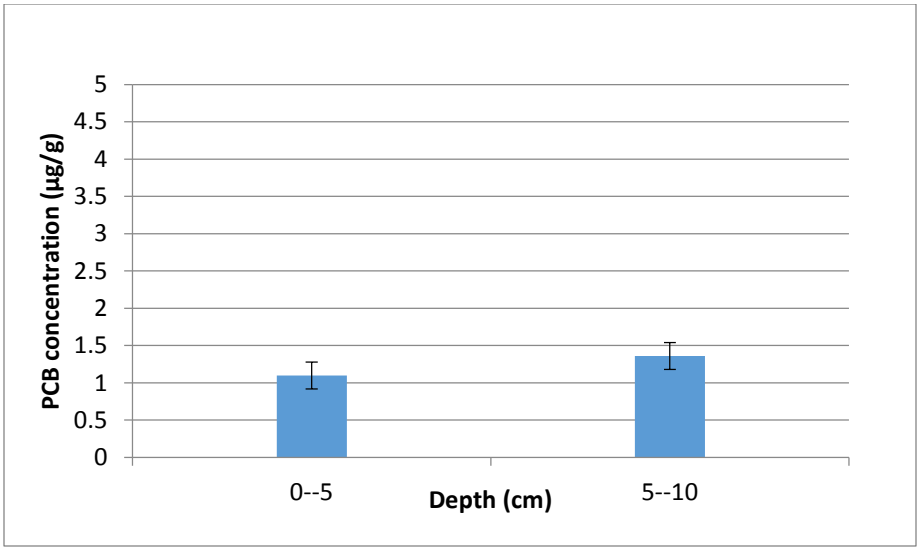


Figure 4.18. Section wise PCB concentration at BH-4. Error bars display the standard error (n=2).

4.3.5 PCB concentration at BH-5

The measured PCB concentration at BH-5 (Figure 4.19) agreed with the general trend of PCB concentration increasing downstream. The calculated average PCB concentration of both sections was 1.96 µg/g. BH-5 is located very close to the location SD011 (see Figure 3.1). SD011 was the area with highest PCB concentration in the study area of the lake. The proximity of BH-5 to SD011 supports this high PCB concentration. Also, as discussed in section 4.2, the particle size analysis of BH-5 predicted a high PCB concentration due to significantly large amounts of clay and silt found in the sediment sample.

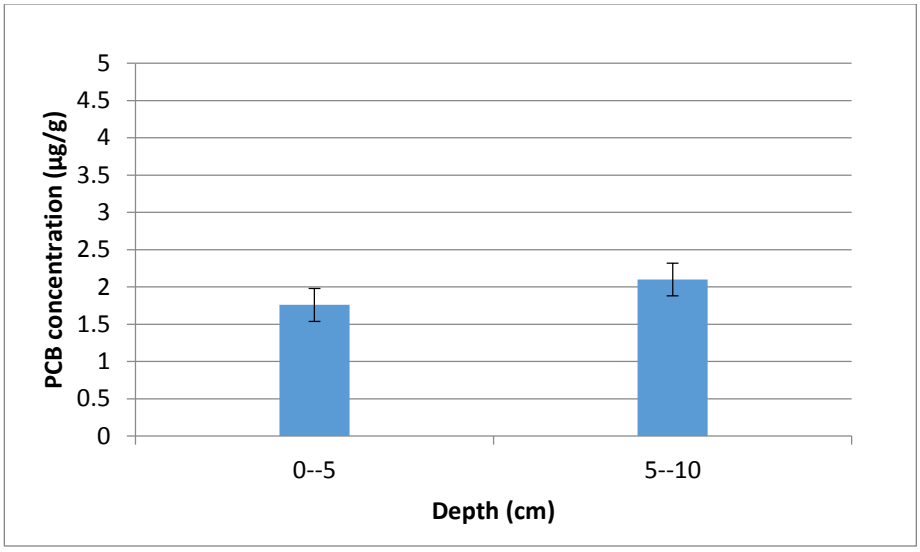


Figure 4.19. Section wise PCB concentration at BH-5. Error bars display the standard error (n=2)

4.3.6 PCB concentration at G-30

G-30 is located further down gradient of BH-5 and is closer to the SD011 sampling point. The total PCB concentration was 3.79 µg/g. The similar location of the two points coupled with the high silt and clay content (see particle size analysis of G-30 in section 4.2) justifies its high PCB concentration. Section wise PCB analysis of G-30 could not be conducted due to constant collapsing of sediment core at this location. To counter this problem, a dredge sampler was used to collect the top 10 cm of sediment from the spot. Figure 4.20 displays the total concentration.

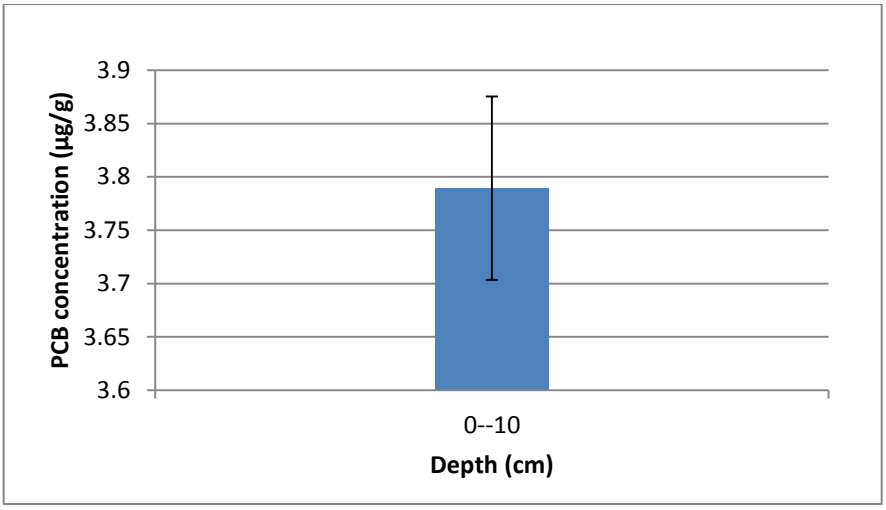


Figure 4.20. PCB concentration of top 10 cm at G-30. Error bars display the standard error (n=2).

Overall, the measured PCB concentrations were considerably above the EPA recommended clean up requirement level of 1µg/g level (USEPA, 1994). BH-3, BH-5 and G-30 showed a spike in PCB concentration which is significantly above the EPA recommended level. BH-1 and BH-2 are well within the EPA recommended level of 1µg/g, with BH-4 approaching 1 µg/g.

4.3.7 Spatial interpolation of congener specific analysis PCB concentration

An important objective of this thesis was to calculate the PCB concentration in the entire arm of the lake. Therefore, the PCB concentration from the congener specific analysis was consolidated into a GIS map and the IDW technique was performed on the layer, with the digitized polygon used

in Figures 4.2 through 4.7 as the boundary. Figure 4.21 displays the result obtained for 2015 using the IDW technique with the measured values for samples collected in 2015.

The PCB concentration distribution was very similar to the PCB concentration in 2013 as shown in Figure 4.6. Sites G-30 and BH-3 can be compared to SD011 and SD009, respectively, in Figure 4.6 due to very similar location. In 2015 (Figure 4.21), G-30 had the highest PCB concentration followed by BH-5 and BH-3 in the same range, whereas in 2013 (Figure 4.6), SD011 had the highest PCB concentration followed by SD009.

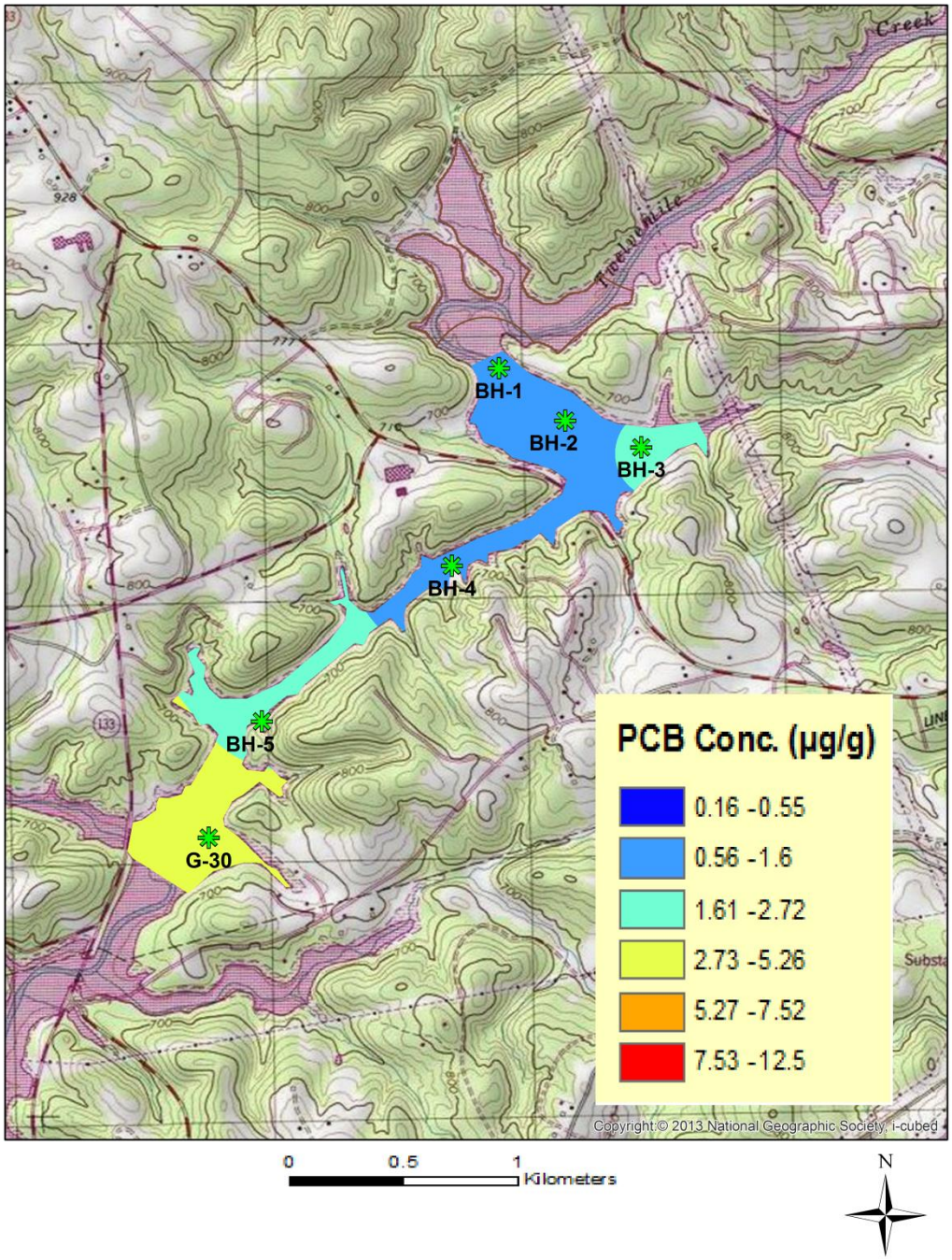


Figure 4.21. Estimated PCB concentration (µg/g) in 2015 using IDW and congener specific analysis of samples in 2015.

4.4 Comparison of the two estimation methods with the congener specific analysis

Another important objective of this thesis was to evaluate the two estimation techniques used, particle size analysis and least squares linear regression. While the two estimation techniques predicted different PCB concentrations for the year 2015, these techniques can be compared with the congener specific analysis to determine if the estimation techniques are effective. Table 4.3 includes the calculated values by all the three methods.

Table 4.3 PCB concentration from the estimation and validation techniques (all data are from 2015)

Site	PSA*	Regression combined with IDW	Congener specific quantification
BH-1	1.25	0.69-1.30	0.69
BH-2	1.50	0.69-1.30	0.77
BH-3	1.73	0.69-1.30	1.69
BH-4	1.00	0-0.68	1.13
BH-5	2.25	0-0.68	1.56
G-30	4.75	0-0.68	3.79

* Particle Size Analysis

The results from the particle size analysis and the congener specific analysis showed the same trend of PCB concentration, and the values matched well. However, the results from the regression combined with IDW

technique did not match up with the congener specific analysis. For BH-1, the GC measured value was at the low end of the range estimated using regression combined with IDW. The particle size estimation provided a higher concentration than the measured value. The difference in results could be due to various uncertainties involved in the procedures. The congener specific analysis has numerous steps right from spiking the sample and extracting it, till analyzing the extracts in the GC-ECD. The treatment of the extracts to remove impurities and the nitrogen blow down were potential steps for error. The magnitude of error associated the congener specific analysis is likely lesser than the error associated with the particle size analysis that was based on a single sample from 2004. Also, the error associated with the IDW and regression analysis is likely greater that the error using the GC analysis.

The result from the regression/IDW technique affects the accuracy in predicting the concentration at a particular spot as it provides a range of PCB concentrations of the area. The concentrations down gradient do not match up well with the measured concentrations. One possible reason for this significant difference in values could be the removal of the Woodside-I and -II dams which affected the rate of transport of sediment downstream post-

2011. The regression technique did not take into this into account while calculating the PCB concentration for the year 2015.

Overall, the particle size analysis predicted a rise in PCB concentration for the year 2015 when compared to preceding years. The regression technique predicted a decrease in PCB concentration. Since the PCB concentration did increase at all sampled locations, the particle size analysis can be concluded as a more effective technique for rapid estimation of PCB concentration than the regression.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

This thesis paved the way for a new perspective of PCB concentration interpretation. The use of GIS and the IDW technique not only provided a more comprehensive understanding of the concentration trends over the years, it estimated the PCB concentration of the entire study area with just a few sample points. This technique has the potential to provide more insight with a minimum number of samples, saving time and money.

The particle size analysis was another estimation technique used to determine PCB concentrations in the sediment. Sediment analysis using GC is an expensive and laborious technique. The hypothesis that PCB concentration is directly proportional to the clay and silt content of the sediment makes particle size analysis a rapid PCB estimation technique aimed at saving both time and money.

The GC analysis of PCBs is an extensive process and involves many procedures that require an experienced analyst. The congener specific GC analysis of the sediment sample still remains the most accurate method for

measuring the total PCBs in the sediment. The increase in overall PCB concentration after the dam removal proved to be an interesting occurrence and was accurately predicted by the particle size analysis method.

Overall, the EPA recommended method of natural attenuation appears to be achieving its goal with PCB concentration decreasing over the years with the concentration upstream having already approached the EPA recommended level of 1 µg/g. The particle size analysis indicated that sand which contained the least PCB contamination was deposited in the upstream portion of the Twelve Mile Creek arm of the lake.

5.2 Recommendations

The two estimation techniques used as part of this thesis are both powerful techniques which with a few alterations to certain parameters can yield far more accurate results. Firstly, to increase the efficiency of the IDW technique, the sampling points need to be well spaced as this improves the efficiency of all spatial interpolation techniques. Secondly, the reason for the failure of superior techniques such as kriging and natural neighbor was the lack of the optimum number of sampling points. For these techniques to work on a large area such as the Twelve Mile Creek arm, more locations should be sampled. The particle size analysis involves a lot of mechanical

work, thereby increasing the possibility of errors. Though the loss of sample mass after the analysis was determined to be less than 0.2%, there is scope for increased efficiency by using parafilm on the outer walls of the sieves to reduce the loss of smaller particles when the sieves are separated. Another improvement could be the use of a sieve shaker which will reduce the labor of breaking down larger sediment conglomerates, and increase the particle separation due to higher speed of agitation. A better technique for the prediction of PCB concentration in the future years would be to develop a fate and transport model of the Twelve Mile Creek arm that includes factors such as sedimentation rate, water flow rate and PCB reductive dechlorination rate on the lines of the model created by Farley et al.(1994).

This project can be continued every year to record the change in PCB concentrations at the same locations and analyze the shift of high PCB concentration points. Sediment traps can be used at strategic locations to validate deposition of finer sediment where higher PCB concentrations were observed. The methods used in this project could be utilized to estimate the PCB concentration in the tissues of fish present in the arm of the lake to predict the biomagnification of PCBs from benthic macro-invertebrates to the fish. Ultimately, the prediction and spatial interpolation techniques can

be used to identify hot spots of maximum PCB contamination in the fish and determine if there is a direct correlation between the tissue PCB concentration and the sediment PCB concentration of that location. Ultimately, these techniques may be used to predict the time required for the PCBs in the fish tissues to reach the FDA recommended safe level for consumption.

APPENDICES

APPENDIX- A

2015 Peak Assignments

Sivey (2005) updated the PCB peak assignment compiled by Frame (1997). Frame did extensive research to assign peaks for all 209 congeners using relative-retention time (RRTs). Sivey (2005) updated the method in an attempt to increase the accuracy of congener specific analyses by identifying 128 congeners in 82 peaks based on RRTs. In an attempt to identify peaks in my calibration standards, I have updated the peak assignment list made by Sivey (2005). While, Sivey (2005) observed 82 peaks attributed to 128 congeners, I found 84 peaks attributed to a total of 130 congeners. Table 4.3 contains the peak identification list developed based on weight percentage calculated in Frame (1997). The minor difference observed between the Sivey (2005) peak assignments and the 2015 peak assignments are the order of elution of peak 30 and the presence of congener 204 which was used as the Internal Standard (I.S)

Table 4.3. 2015 Peak assignments.

Peak #	**Congeners**	**RetTime**	**RRT Aldrin**	**RRT PCB 204**	**1:1 Mix Wt%**
1	4, 10	15.5909	0.5769	0.3190	1.995
2	9, 7	16.6273	0.6152	0.3402	0.441
3	6	17.1131	0.6332	0.3502	0.838

4	8, 5	17.3949	0.6436	0.3559	4.275
5	19	18.4299	0.6819	0.3771	0.500
6	12	19.4783	0.7207	0.3986	0.035
7	13, 18	19.6755	0.7280	0.4026	5.608
8	17, 15	19.8003	0.7326	0.4052	3.248
9	24, 27	20.3327	0.7523	0.4161	0.336
10	16, 32	20.8874	0.7729	0.4274	3.168
11	34, 23	21.4794	0.7948	0.4395	0.023
12	54, 29	21.7809	0.8059	0.4457	0.058
13	26	22.1290	0.8188	0.4528	0.798
14	25	22.3204	0.8259	0.4567	0.360
15	31	22.7655	0.8424	0.4658	4.743
16	28	22.8704	0.8462	0.4680	4.330
17	20, 33, 53	23.6644	0.8756	0.4842	4.109
18	51	24.1493	0.8936	0.4942	0.160
19	22	24.3189	0.8998	0.4976	1.768
20	45	24.7665	0.9164	0.5068	0.630
21	46	25.4560	0.9419	0.5209	0.243
22	43, 52	25.8219	0.9555	0.5284	3.996
23	49	26.2028	0.9696	0.5362	2.028
24	48	26.4480	0.9786	0.5412	0.843
25	47, 75	26.5422	0.9821	0.5431	0.708
26	**aldrin**	27.0256	1.0000	0.5530	-
27	35	27.2612	1.0087	0.5578	0.028
28	44	27.6504	1.0231	0.5658	2.983
29	59, 42, 37	27.9462	1.0341	0.5719	1.586
30	71	28.6365	1.0596	0.5860	0.648
31	41, 64	28.7456	1.0636	0.5882	1.553
32	96	29.1605	1.0790	0.5967	0.033
33	40, 103, 57	29.4696	1.0904	0.6030	0.371
34	67	29.9704	1.1090	0.6133	0.030
35	63, 94	30.4758	1.1277	0.6236	0.055
36	74	30.8193	1.1404	0.6306	0.923
37	70	31.1680	1.1533	0.6378	2.868
38	76, 102	31.3618	1.1604	0.6418	0.093
39	95, 66	31.5634	1.1679	0.6459	3.505
40	91	32.1323	1.1890	0.6575	0.395
41	56, 60	33.0043	1.2212	0.6754	0.895
42	92	33.1389	1.2262	0.6781	0.465
43	84, 86	33.4602	1.2381	0.6847	1.040
44	101, 113	33.6493	1.2451	0.6886	3.400
45	99	34.1159	1.2624	0.6981	1.893
46	119	34.6926	1.2837	0.7099	0.050
47	83	35.1118	1.2992	0.7185	0.260

48	97, 86, 125	35.5800	1.3165	0.7281	1.413
49	87, 115, 117	36.0469	1.3338	0.7376	2.098
50	85	36.4181	1.3475	0.7452	0.943
51	136	36.6644	1.3567	0.7503	0.235
52	77, 110, 154	36.9398	1.3668	0.7559	4.501
53	82	37.9348	1.4037	0.7763	0.660
54	151	38.0428	1.4077	0.7785	0.228
55	135, 144, 124	38.4446	1.4225	0.7867	0.503
56	109, 147	38.8447	1.4373	0.7949	0.318
57	139, 149, 123	39.1234	1.4476	0.8006	1.559
58	118	39.2764	1.4533	0.8037	5.235
59	134	40.0429	1.4817	0.8194	0.143
60	114, 133	40.2459	1.4892	0.8235	0.198
61	131, 122	40.4224	1.4957	0.8272	0.171
62	146	40.7914	1.5094	0.8347	0.280
63	153	41.3210	1.5290	0.8455	1.765
64	132	41.5303	1.5367	0.8498	0.948
65	105	41.6211	1.5401	0.8517	2.590
66	141, 179, 137	42.4372	1.5703	0.8684	0.683
67	176, 130	43.0384	1.5925	0.8807	0.285
68	164, 163	43.2810	1.6015	0.8856	0.611
69	138	43.7558	1.6190	0.8954	2.938
70	158	43.9627	1.6267	0.8996	0.428
71	178, 129, 126	44.4493	1.6447	0.9096	0.206
72	166	44.9905	1.6647	0.9206	0.025
73	187	45.2537	1.6745	0.9260	0.085
74	183	45.6917	1.6907	0.9350	0.068
75	128	46.1375	1.7072	0.9441	0.783
76	167	46.2570	1.7116	0.9465	0.155
77	174	47.2849	1.7496	0.9676	0.120
78	177	47.7489	1.7668	0.9771	0.070
79	156, 171	48.2215	1.7843	0.9867	0.543
80	157	48.7171	1.8026	0.9969	0.123
81	**204**	48.8692	1.8083	1.0000	-
82	172	49.1518	1.8187	1.0058	0.025
83	180, 193	49.7068	1.8392	1.0171	0.281
84	170, 190	52.2032	1.9316	1.0682	0.248

APPENDIX-B

GC calibration standards preparation procedure

Materials

1. Standard stock solutions were purchased at a concentration of 100 µg/mL in 1 mL vials.
    a. Aroclor 1016, Aroclor 1254, and aldrin stock solutions are prepared in methanol
    b. PCBs 14, 169, and 204 are prepared in isooctane
    c. After opening, add to an amber glass vial. Weigh vial before and after to know how much is in there for future use.
2. Solvent used for dilution is isooctane (Density 691.94 mg/mL at 20℃)

. Density of methanol is 791 mg/mL at 20℃? and 786.6 mg/mL at 25℃

a. *Lab temp should be 20-25℃ so any density between that temp range is suitable*

b. Make a note of the temperature of the lab when preparing standard solutions

3. Syringes (25 µL, 250 µL, and 1 mL)

Between each use, the syringes should be cleaned by rinsing it with methanol 3 times for the first dilution and with isooctane 3 times when making the series of dilutions

4. Five 10 mL volumetric flasks and one 20 mL volumetric flask
5. Six ~20 mL amber glass vials with solid, teflon caps

Objectives

1. Calibration standards of a 1:1 mixture of Aroclor 1016 and 1254 should be diluted to 5 concentrations: 100, 250, 500, 1000, and 2000 ng/mL (total PCB concentrations; Sivey (2005))
2. Standard calibration preparation needs to be completed in one day
3. Internal standard solution of aldrin at 36 ng/mL and PCB 204 at 36 ng/mL
4. Recovery standard solution of PCBs 14 and 169
5. Calculate actual concentration of all solutions by carefully massing all equipment and using density of isooctane (or methanol depending on what solvent the purchased stock solution is made with)

Procedures

Internal Standards (IS) Preparation:

1. Add 18 µL of aldrin and 18 µL of PCB 204 stock solutions (100 µg/mL each) to a 10 mL volumetric flask and dilute with isooctane
    - This produces a solution with a nominal concentration of 180 ng/mL aldrin and 180 ng/mL PCB 204
    - Label standard solution with name, concentration, and date
    - Place mark at level of solution so that loss by evaporation can be detected
    - Solutions should be made fresh every 6 months and stored in vials capped with teflon lids in the fridge prior to use.

To determine the actual concentration:

- Weigh the empty syringe (at the end you will know how much is left in the syringe after injecting)
- Uptake IS with syringe and then weigh syringe
- Weigh syringe directly after adding IS

- *Neither MeOH nor isooctane will evaporate quickly so it is not necessary to use a cap or parafilm on the flask to prevent evaporation*

i. Using the density of the solvent (MeOH or isooctane) and the difference in weight of the syringe, the actual volume of IS added can be calculated

- The weight of the IS added multiplied by its density will give the actual volume added.

ii. This must be performed for all prepared solutions including PCB calibration dilution series and preparations used for GC analysis

<u>PCB Calibration Dilution Series</u>

1. Add 250 µL of Aroclor 1016 and 250 µL of Aroclor 1254 stock solutions (100 µg/mL each) to a 20 mL volumetric flask and dilute with isooctane
    - This makes a nominal concentration of 2500 ng/mL total PCB (Aroclor 1016+1254)
2. Transfer 5 mL of the 2500 ng/mL solution to a 10 mL volumetric flask and dilute with isooctane

- This makes a nominal concentration of 1250 ng/mL total PCB

3. Transfer 2.5 mL of the 2500 ng/mL solution to a 10 mL volumetric flask and dilute with isooctane
    - This makes a nominal concentration of 625 ng/mL total PCB
4. Transfer 1.25 mL of the 2500 ng/mL solution to a 10 mL volumetric flask and dilute with isooctane
    - This makes a nominal concentration of 312.5 ng/mL total PCB
5. Transfer 0.5 mL of 2500 ng/mL solution to a 10 mL volumetric flask and dilute with isooctane
    - This makes a nominal concentration of 125 ng/mL total PCB

GC Analysis (Agilent 6890 ChemStation Rev. B.01.01 [164])

1. Samples
    - Transfer 1000 µL of the 2500 ng/mL total PCB solution to a GC vial. Add 250 µL of the 180 ng/mL internal standards solution (aldrin/PCB204) to the GC vial, bringing the total volume to 1.25 mL

        - This will produce a nominal total PCB concentration of 2000 ng/mL and a nominal internal standard concentration of 36 ng/mL
    - Repeat the same procedure with the 1000µL:250µL ratio of PCB:IS for all dilution concentrations of the PCB dilution series and it will produce the desired concentrations of 2000, 1000, 500, 250, and 100 ng/mL.

2. Instrument Method (GC-ECD) - taken from Sivey (2005)
    - Analyzed on Hewlett-Packard 6890 GC equipped with 60m fused silica capillary column: RTX-5; 0.25 mm diameter, 0.25 µm film thickness and a ^{63}Ni electron capture detector
    - Samples analyzed via duplicate injection

APPENDIX C

PCB concentrations at SD points from 1995 to 2013 compiled by URS Corporation for SCDHEC.

	SD000	SD001	SD002	SD003	SD004	SD005	SD006	SD007	SD008	SD009
1995		0.821	2.32	0.059	1.54	0.522	0.943	1.58	3.07	
1996	0.065	1.31	0.977	0.112	1.28	1.5	0.159	4.26	0.686	5.67
1997	0.065	1.56	1.85	0.085	0.392	2.36	0.235	1.46	2.13	4.71
1998		0.0765	0.229	0.0725	0.764	0.51675	0.255	0.283	0.0705	2.62
1999	0.0325	2.18	0.404	0.03	1.16	0.137	0.308	0.228	2.695	3.21
2000	<0.0653	0.617	3.87	<0.0663	0.373	0.23	0.0675	0.0603	1.63	2.515
2001	<0.0638	2.56	0.683	<0.130	1.07	0.367	0.5835	0.218	0.472	2.465
2002	<0.105	1.85	1.2	<0.135	0.36	0.163	0.864	0.075	0.063	4.26
2003	<0.0649	<0.0684	0.0988	0.0628	0.0794	0.0638	0.0604	0.0629	0.0621	3.26
2004	<0.0791	0.695	0.07	<0.0640	0.182	0.478	0.119	2.35	0.0632	4.07
2005	<0.033	0.19	0.34	<0.031	0.3	0.03	0.22	2.3	0.37	2.2
2006	<0.069	1.1	3.4	<0.035	2.05	0.11	1.1	2.6	2.2	3.5
2007	<0.016	0.31	0.73	<0.016	0.26	0.14	0.12	0.084	0.19	0.28
2008	0.0308	0.487	0.52	<0.024	0.602	0.474	0.113	0.0723	0.125	2.07
2009	<0.024	0.05	0.804	<0.034	0.132	0.034	1.73	0.033	0.034	0.73
2010	<0.007	0.091	0.385	<0.033	0.5	0.0231	0.156	0.085	0.89	1.32
2011	<0.024	0.0388	0.189	<0.024	0.096	0.024	0.075	0.024	0.086	0.543
2012	<0.0318	0.0467	0.724	<0.034	0.218	0.077	0.0298	1.9	0.273	0.748
2013	<0.033	0.105	0.852	<0.032	0.594	0.635	0.03	0.181	0.163	2.25

	SD010	SD011	SD012	SD013	SD014	SD015	SD106	SD532	SD535
1995	8.56	16	12	23.3	1.7	0.678	8.92	0.578	1.83
1996	3.12	6.53	5.81	8.26	5.17	1.62	5.65	0.454	0.235
1997	3.78	6.51	4.12	8.6	1.39	2.09	4.1	0.385	0.512
1998	2.05	2.83	2.53	2.25	1.31	1.03	0.514	0.881	0.137
1999	3.06	3.93	2.195	5.78	1.4	2.99	3.46	0.405	0.837
2000	2.08	12.5	1.33	1.97	1.18	0.518	2.36	0.209	0.62
2001	2.6	2.32	5.73	3.98	0.814	0.445	0.487	0.191	0.398
2002	5.55	3.3	1.92	9.68	0.896	0.539	2.93	0.1765	0.579
2003	0.33	2.27	1.77	5.51	0.642	1.61	1.305	0.181	0.169
2004	0.513	2.035	1.72	2.48	0.693	0.507	1.41	0.2	0.282
2005	0.082	1.95	0.74	5.8	0.675	0.68	1.9	0.26	0.35
2006	1.9	2.1	2.1	2.4	0.71	0.8	2.9	0.48	1
2007	0.48	0.27	0.26	0.26	0.22	0.1	0.44	0.051	0.24
2008	3.15	0.968	1.09	1.22	0.633	0.637	3.1	0.316	0.416
2009	0.175	1.12	0.582	0.284	0.08	0.078	1.08	0.088	0.115
2010	1.24	1.76	1.06	1.68	0.3	0.29	1.36	0.185	0.23
2011	0.183	0.761	0.376	0.41	0.15	0.234	0.22	0.061	0.117
2012	1.39	2.22	1.01	1.01	0.57	0.375	1.08	0.0922	0.473
2013	0.117	3.96	1.4	0.591	0.454	0.527	0.661	0.112	0.113

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